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Workshop and Report on Implications of Bio-refineries for Energy and Trade in the APEC Region

APEC 21st Century Renewable Energy Development Initiative (Collaborative IX)
November 2009, Chinese Taipei

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Nexant

ITRI
Industrial Technolog
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Workshop and Report on Implications of Bio-refineries for Energy and Trade in the APEC Region

(EWG 05/2008A)

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Table of Contents

Section Page

Acknowlegment

Appendix

List of Figures

Figure Page

List of Tables

Acronyms

ABE – Acetone-Butanol-Ethanol

ABR – Anaerobic Baffled Reactor

ADM – Archer Daniels Midland Company

AFAD – Attached Film Anaerobic Digestion

AMFE/AFEX – Ammonia Fiber Explosion

APR – Aqueous-Phase Reforming

ARP – Ammonia Recycle Percolation

ASTM – American Society for Testing and Materials

ATAD – Aerobic Thermophilic Autothermal Digestion

ATTM – Ammonium Tetrathiomolybdate

BIG-FT – Biomass Integrated Gasification Fischer-Tropsch

BOD – Biochemical Oxygen Demand

BTL – Biomass-to-Liquids

CAFI – Consortium for Applied Fundamentals and Innovation

CAFO – Concentrated Animal Feeding Operation

CHP – Combined Heat and Power

CNG – Compressed Natural Gas

COD – Chemical Oxygen Demand

CRP – Conservation Reserve Program

CSTR – Continuous Stirred Tank Reactor

CTL – Coal-to-Liquids

DDGS – Dried Distiller Grains with Solubles

DME - Dimethylether

DOE/USDOE – United States Department of Energy

EERE – Office of Energy Efficiency and Renewable Energy (United States)

EFB – Empty Fruit Bunches

ETG – Ethanol-to-Gasoline

EPA/USEPA – United States Environmental Protection Agency

FAEE – Fatty Acid Ethyl Esters

FAME – Fatty acid methyl ester

FAO – Food and Agricultural Organization

FCC – Fluid Catalytic Cracking

FFA – Free Fatty Acids

FOG – Fats, Oils and Greases

F-T – Fischer-Tropsch

GHG – Greenhouse Gas

GHSV – Gas Hourly Space Velocity

GTI – Gas Technology Institute

GTL – Gas-to-Liquids

GTL – Genomics-to-Liquids

HAS – Higher Alcohol Synthesis

HAP – Hydroxyapatite

HDPE – High Density Polyethylene

HDO – Hydro-de-oxygenation

HFCS – High Fructose Corn Syrup

HMF - Hydroxymethylfurfural

HRT – Hydraulic Retention Time

HTU - HydroThermalUpgrading

IFP – Institut Francais de Petrole

INEEL – Idaho National Engineering and Environmental

KWTE – Korat Waste to Energy Company

LCA – Life Cycle Inventory and Assessment

LFG – Landfill Gas

LHV – Lower Heating Value

LNG – Liquefied Natural Gas

LPG – Liquefied Petroleum Gas

MFT – Mobilized Film Technology

MRF – Materials Recovery Facility

MSW – Municipal Solid Waste

MTG – Methanol-to-Gasoline

MTBE – Methyl Tert-Buty Ether

MTHF – Methyltetrahydrofuran

MVR – Mechanical Vapor Recompression

NEDO – New Energy and Industrial Development

NMOC – Non-methane Organic Compounds

NREL – National Renewable Energy Laboratory

PET – Polyethylene Terephthalate

POTW – Publicly Owned Treatment Works

POX – Partial Oxidation

PRIME – Pierre Renewable Integrated Meat & Energy

ROI – Return on Investment

RTP – Rapid Thermal Processing^{TM}

RFS – Renewable Fuel Standard

SSL – Small Scale Liquefaction

SWI – Sanguan Wongse Industries

SWOT - Strengths, Weaknesses, Opportunities, and Threats Analysis

TAPPI – Technical Association of the Pulp and Paper Industry

TCC – Tube Cooled Converter

TS – Total Solids

TSS – Total Dissolved Solids

TVA – Tennessee Valley Authority

UASB – Upflow Anaerobic Sludge Blanket

ULSD – Ultra Low Sulfur Diesel

USGC – United States Gulf Coast

WDGS – Wet Distillers Grains and Solubles

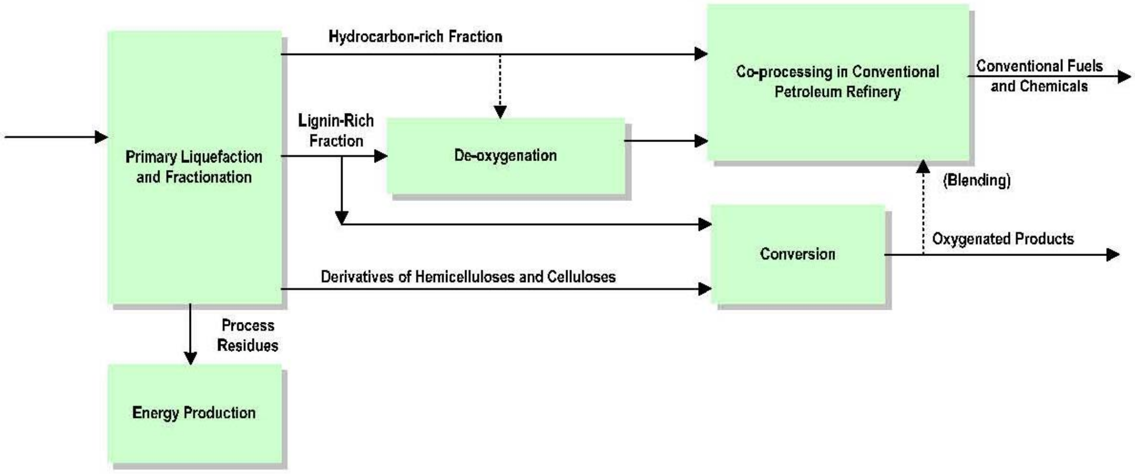
WTE – Waste-to-Energy

1.1 INTRODUCTION

This report introduces the emerging "second generation" biofuel technologies such as bio-refinery technologies with feedstocks from non-food biomass. It also includes the technical and commercial applications of the "first generation" biofuel technologies with most of the feedstocks from food crops, such as corn ethanol in the United States, sugarcane ethanol in Brazil, and fatty acid methyl ester (FAME) biodiesel. A Workshop on Implications of Energy and Trade in the APEC Region was held on 7-9 October, 2009 in Chinese Taipei bringing together experts and engineers involved in the development of bio-refinery technologies to discuss the bio-refinery technologies for making hydrocarbon biofuels a practical reality in the future. Presentations and discussions of the workshop are to articulate the suggested biofuels trade and the critical role that chemistry, chemical catalysts, thermal processing, and engineering play in the conversion of lingo-cellulosic biomass into biofuels.

The notion of a bio-refinery is comparable to current petroleum refineries where various fuels and products are created from petroleum. The petroleum refinery takes crude oil and fractionates all of the prospective molecular feedstocks for additional processing and blending to generate many different fossil fuel based products. Figure 1.1 shows a generalized process flow diagram of this bio-refining concept. The bio-refinery facility incorporates biomass conversion equipment and processes to generate fuels, power, and chemicals from a biomass feedstock. The facility is able to utilize and maximize the value of the different components in the biomass feedstocks and intermediates. The figure demonstrates how biomass conversion technologies can be integrated into traditional petroleum based refineries and thus creating a bio-refinery.

Figure 1.1 Overall Bio-refining Concept



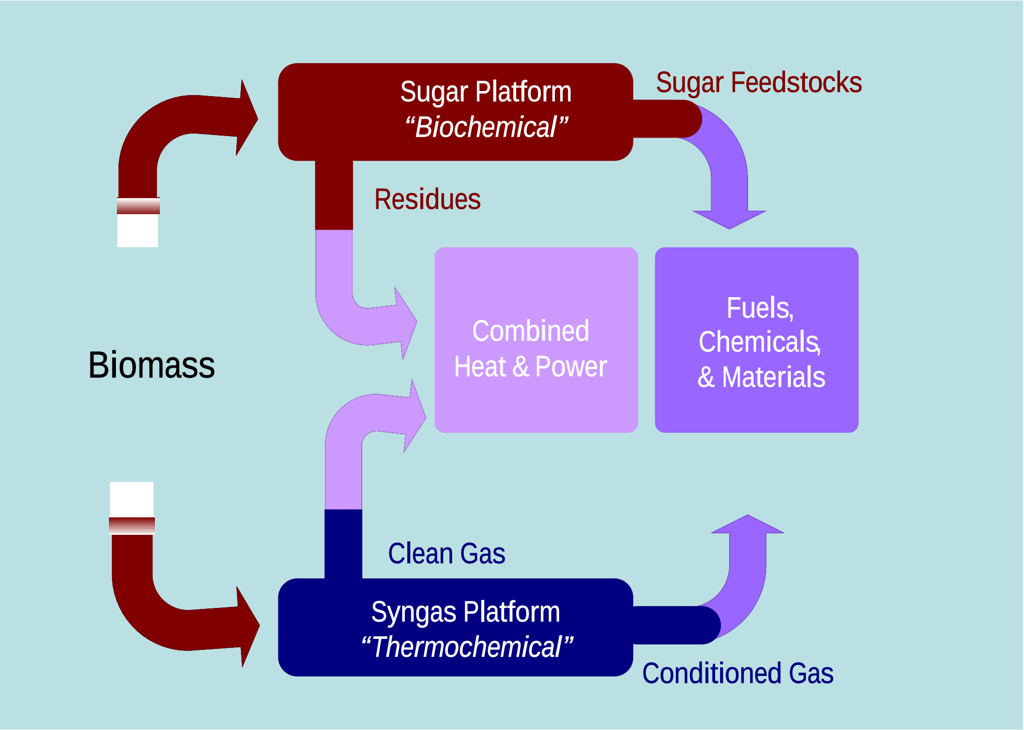
Source: Yrjo Solantausta, 14.3.2006, VTT

Integrated bio-refineries apply many different arrangements of feedstocks and conversion technologies to make various products, with an emphasis on generating biofuels. Some of the side products might include chemicals (or other materials), heat and power. A few of the renewable feedstocks used in the integrated bio-refineries could be grains, such as corn, wheat sorghum and barley, energy crops like switchgrass, miscanthus and willow, and agricultural, forest and industrial residues such as bagasse, stover, straws, sawdust and paper mill waste.

There are a variety of bio-refinery concepts in the research and development stage. The concept of "Whole Crop Bio-refinery" utilizes raw materials such as cereals or corn. The "Green Bio-refinery" is able to process materials with reasonably high water content, like green grass, clover, or immature cereals. The "Lignocellulose Feedstock Bio-refinery" makes use of nature-dry raw materials with high cellulose content, such as straw, wood, and paper waste.

The bio-refinery concept, developed by the National Renewable Energy Laboratory (NREL), breaks up the facility into two different "platforms" in order to get the most out of the product line-ups. The platforms split bio-refinery technologies into two categories, Biochemical and Thermochemical. Figure 1.2 displays NREL's two category bio-refinery concept. Nexant has adopted this method of categorization for bio-refinery technologies and has such organized the following report in this manner.

Figure 1.2 NREL Bio-refinery Concept



Source: NREL

The basis for the biochemical platform is the biochemical conversion processes which concentrate on the fermentation of sugars that are taken from the biomass feedstocks. This platform ferments the carbohydrate content of biomass into sugars that can then be processed to make fuels, chemicals, and other materials. The foundation of the thermochemical platform is the thermochemical conversion processes that center on the gasification of biomass feedstock and the by-products from the conversion processes. The thermochemical process uses pyrolysis or gasification to process the biomass feedstock to generate a hydrogen rich synthesis gas that can then be utilized in various chemical processes.

A bio-refinery has the ability to create one or more low volume, but high value, chemical products and a low value, but high volume liquid transportation fuel. At the same time, it can also make electricity and process heat for its own use and sell a portion of the electricity in some instances. High value products boost profitability for the facility and the fuels produced in bulk volumes would help meet the national energy needs of the economy. The power generated within the bio-refinery will reduce energy costs and help lessen the emissions of greenhouse gases.

Integrated bio-refineries have many benefits because of the diverse feedstocks used and products produced. Currently, bio-refineries have a number of different levels of integration which increases its sustainability, economically and for the environment. A few bio-refinery concepts only generate ethanol or biodiesel while others fully integrate livestock farming or heat and power and other bio-based products. A number of these refineries are self-sustaining with respect to energy consumption.

1.1.1 Bio-refinery Technology Challenges

“Bio-refinery technology”, for both conventional as well as next generation technologies, represents a number of diverse aspects and developmental challenges along the product value chains. These are primarily categorized as follows:

- Plant Biotech (crop genetics)
    - Improving land yields of existing crops for sugars, starches, oils, and/or biomass, with less agronomic inputs, better quality products
    - Developing new crops for higher yields or improved types of sugars, starches, oils, and/or biomass (e.g., energy cane, jatropha, etc.)
- Microbial biotech
    - Developing better, more cheaply produced grain and cellulosic biomass liquefaction/saccharification enzymes for exogenous use or microbes for these tasks, and better fermentation microbes for biofuels production, such as for ethanol or butanol fermentations, especially for utilizing C_5 sugars
    - Microbial routes to other alcohols and other biofuels (especially bio-hydrocarbons) from sugar or cellulosic substrates
    - Fermentation of carbon monoxide (bio-syngas) to alcohols, etc.
    - Improved microalgae strains to overcome conventional physical limitations and challenges
- Bioprocess improvements – other than biotech

  - Faster, cheaper, more compact physical/chemical pretreatments
  - Lignin separation and use
  - More efficient distillation and dehydration (e.g., for ethanol)
  - Improved fatty acid esterification (e.g., by heterogeneous catalysts)
  - Recovery of biodiesel co-product glycerin
  - Less production of by-products and residues
  - Biomass energy supply and recovery (e.g., by biodigestion, gasification, etc.)
  - Improved growing regimes and cell concentration and oil separation techniques for microalgae systems

- Chemical process improvements – applications of conventional thermo-chemical and catalytic processing to biomaterials
  - Partial oxidation gasification of biomass (pyrolysis)
  - Hydrocracking and isomerization of natural fats, oils, and greases to fuel hydrocarbons
  - Steam catalytic cracking of biomass, oils, and/or alcohols using FCC-like processing
  - Fischer-Tropsch catalysis of biosyngas to make gasoline or diesel fractions, higher alcohols, etc.

- Novel departures from the all of the above, including to date:
  - Catalytic conversion of sugars in solution to hydrocarbons or hydrogen
  - Fermenting sugars to lipids using algae species (non-photosynthetic)
  - Fermenting sugars directly to hydrocarbons for conversion to gasoline, diesel, jet fuel, and/or substitutes for common petrochemicals
  - Derivatization of chemicals or fuels from alcohols (e.g., methanol-to-gasoline, ethanol-to-gasoline, ethylene, butadiene, *n*-butanol, etc.)
  - Algae production of ethanol
  - Fermentation of sugars to acids, followed by conversion to alcohols

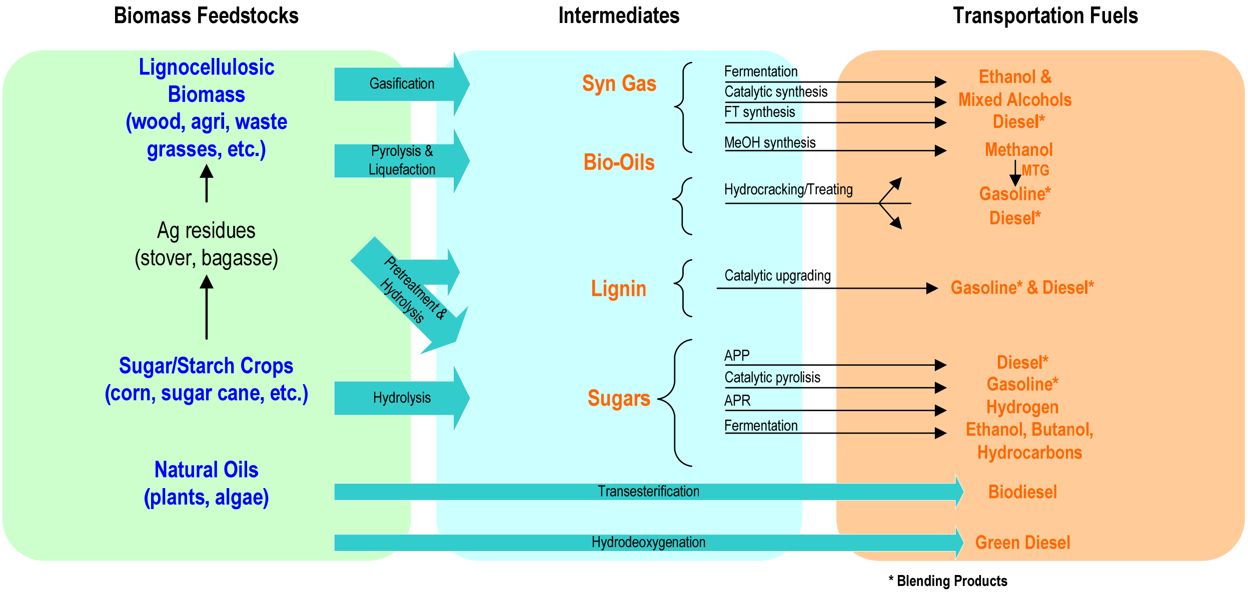
- Distribution and use of biofuels in existing systems
- Disposition of bio-based chemical products as they replace their petroleum based counterparts

1.2 TECHNOLOGY

Bio-refineries employ the use of biomass conversion technology to produce fuels, chemicals, heat and power traditionally generated by petroleum and fossil fuels. The most significant products produced from bio-refineries are biofuels. As the world tries to lower its dependence on petroleum, bio-refinery technologies are taking the lead in ushering in a new era of bio-based products.

There are a number of technologies available or in the developmental stage that produce different types of biofuels, from ethanol to butanol to ester-based biodiesel to hydrocarbons. Ethanol is a good fuel to supplement or substitute for petro-gasoline; however, it has a number of issues ranging from performance characteristics to production costs. It is the only major biologically-derived fuel being used as a substitute for petroleum gasoline in the world today, but there is concern over global limits on the availability of feedstocks. Nexant and many other experts foresee the commercialization of several second generation biofuel products and processes that augment or supplant grain and sugar ethanol as a substitute for gasoline over the next decade, and/or utilize lipids other than by transesterification, alongside the development of third generation biofuels. Figure 1.3 displays the different biofuel options in various technologies that are available beyond the ethanol fermentation route.

Figure 1.3 Transportation Biofuels Process Options



Soure: NREL

Nexant draws the following conclusions from the examination of a number of these liquid biorefinery technology options:

- With the growth in the current mode of ethanol production by fermentation of grain and sugar feedstocks, comprised of corn, wheat, other major coarse cereals, sugarcane and sugar beets, dislocations are likely to occur in world food and feed markets; to avoid these, similar starch and sugar crops such as sorghum and cassava will be further developed in agriculture and processing technology
- An attractive optional solution for extending ethanol production is in using emerging technology to convert biomass wastes such as corn stover, wheat or rice straw, or sugarcane biomass (field waste and bagasse) to fermentable sugars
- The next level of options include making ethanol by fermenting sugars derived from switchgrass or higher-yield “energy cane”, implementation of which will require development of a new agriculture, including extensive new switchgrass origination systems and supply chains, and modification of the current sugarcane agricultural model;

much general and specific attention is being paid to these options (e.g., in the United States and Brazil)

- In the longer term, as ethanol becomes a more significant petroleum replacement, to relieve logistic constraints (whether ethanol is made from grain, sugar or biomass), industry will most likely convert it to hydrocarbon gasoline fractions in integrated facilities, or make higher alcohols such as butanol instead
- Additional longer-term options include biomass gasification to make syngas for catalytic syntheses to produce gasoline fractions or higher alcohols (so-called "biomass-to-liquids" or BTL)
- Biobutanol is already a commercial technology (ABE – clostridium-based fermentative co-production of acetone, butanol, and ethanol) that only needs to be re-instated and improved
- Biobutanol is most likely to be more widely commercialized by taking market share from synthetic butanol in the industrial chemical and solvent markets before it achieves market share as a fuel at lower prices
- Hydrocarbons are the components of gasoline, diesel, and jet fuel; by using synthetic biology to either alter existing microbes or build new ones, these new microbes in fermentations can be made to produce hydrocarbons that directly or through further processing yield fuels that are more compatible with the current infrastructure than alcohols or ester-based biodiesel
- Gasification can be used to convert the by-products and residues from other biofuel processes as well as from the agricultural value chain that supplies these processes and agricultural, forest products, and food processing biomass wastes in general
- The current version of biodiesel, fatty acid methyl ester (FAME), is most likely a "transition" technology, which, though it can make an attractive venture given tax incentives currently in place, ultimately cannot substitute significantly for petroleum diesel in the marketplace because of feedstock limitations orders of magnitude more severe than for ethanol
- Biodiesel made by emerging technologies to hydrocrack triglycerides (fats and oils) in refineries (i.e., NExBTL and H-Bio), has improved potential for economy of scale, more rapid development, makes biodiesel more attractive for refiners' involvement, and integrates better with the refining and vehicle infrastructure, and will likely be adopted widely in the near term
- In the longer term, synthetic diesel from biomass (made via gasification followed by F-T conversion) is likely to be more economic than conventional biodiesel, with low feedstock costs, substantial by-product credits, and great economies of scale - but the product is also essentially as toxic and non-biodegradable as fossil resource-derived diesel fuel
- FCC technology can be used to convert biomass and other biofuels materials to hydrocarbons that are more compatible with petroleum and petrochemical operations and with conventional vehicle fueling systems

- Other technologies that use different methods of producing biofuels include technologies from Virent (Aqueous Phase Reforming), Terrabon (lime pre-treatment, organic acid hydrogenation) and Zeachem (acetic acid fermentation with hydrogenation)
- Bio-refineries will incorporate biomass conversion equipment and processes to produce fuels, power and chemicals from a biomass feedstock, utilizing the value of different components in the biomass feedstocks and intermediates

Other conclusions in respect to APEC member economies include:

- Fermentation of sugar, starch and grain continues to dominate in the US as most commercial scale plants in the area employ this type of technology
- Commercial lignocellulosic ethanol soon may become a reality as several commercial scale lignocellulosic feedstock based bio-refineries are being built in the US
  - Abengoa Bioenergy Biomass, LLC (Hugoton, Kansas) – converting lignocellulosic feedstocks (corn stover, wheat straw, sorghum, switchgrass) to produce both ethanol and syngas, with 11.4 million gallons of ethanol per year. Also co-producing steam for cellulosic ethanol operations and excess steam for corn ethanol plant nearby. Estimated construction and start up in 2010 and 2012, respectively
  - Range Fuels (formerly Kergy Inc.) (Soperton, Georgia) – converting biomass (comprised of unmerchantable timber and forest residues) to produce 935 thousand gallons of ethanol and 935 thousand gallons of methanol. Using pyrolysis followed by thermal reforming of pyrolysis vapors for biomass conversion. Estimated start up is the first quarter of 2010
  - Poet (formerly Broin Companies) (Emmetsburg, Wisconsin) – converting lignocellulosic feedstocks (corn cobs and/or corn fiber) to produce 25 million gallons of ethanol per year. Integrating the production of cellulosic ethanol into a dry corn mill process. Production is estimated to start in 2011
  - BlueFire Ethanol, Inc. (Mecca, California) – converting biomass (comprised of sorted green waste and woody waste from landfills) to produce 19 million gallons of ethanol per year. Using their concentrated acid hydrolysis technology followed by fermentation for biomass conversion. Facility will be located next to a 47MW biomass fed power plant. Project is currently delayed
- Other organizations are reported to be researching lignocellulosic-based ethanol production via fermentation routes or planning projects based on various types of biomass, including Iogen (Canada/United States), Dedini (DHR Process, Brazil), Abengoa Bioenergy (Spain), and BCI (United States)
  - Iogen is successfully operating a facility in Ottawa, Canada using their proprietary enzyme hydrolysis and fermentation techniques on wheat straw feedstock.
  - BCI is building a commercial demonstration plant in Jennings, LA, US. The unique aspect of this company's technology is the genetically modified organism based on an E. coli bacterium with the ethanol production genes of zymomonas

spliced into it. The process is claimed to be ideally suited to handle biomass feedstocks that produce both C_5 and C_6 sugars upon hydrolysis

- In China, Dynamotive Energy Systems is set to support the development of a pyrolysis plant in Henan province, China. The plant will be based of the company's fast pyrolysis technology
- Pyrolysis technology is also used in other APEC member economies such as, Canada, Malaysia and the US. In Malaysia, The Genting Group produced Malaysia's first commercially produced bio-oil from empty palm fruit bunches
- Neste Oil has built an 800 thousand ton per year renewable diesel plant in Singapore based on its NExBTL technology. It is the largest facility worldwide for producing diesel from renewable sources including a broad variety of natural oils and fats. The new plant in Singapore will provide this APEC member economy an opportunity to develop into a center for Asian biofuel production
- Both first and second generation feedstocks are mostly available in APEC member economies. Second generation feedstocks, such as cellulosic biomass, should especially be considered for use by APEC member economies in biorefinery applications as these feedstocks are garnering the most attention
- A large number of other biomass gasification technologies have been proposed and are being developed worldwide, in Europe, Scandinavia, North America, Brazil, India, China, and elsewhere in Asia and in the world. Many of these are too small in scale, too weakly sponsored, are air-blown, or are so focused on power and heat production as to exclude them as candidates to commercially produce syngas for biofuels production in the mid-term

1.3 WATER USAGE FOR ETHANOL PRODUCTION

Water is an integral part of the ethanol production and has become an increasingly important issue as alternative fuels become a more likely solution to the world's energy problems. Nexant has drawn the following conclusions from examination of water usage for ethanol production:

- The two largest consumers of water during the corn ethanol life cycle are water consumption in crop feedstock production and the corn ethanol production process
- Energy and water demands of ethanol processes are closely integrated and one way to reduce water demand is to reduce energy consumption
- Steps to reduce water requirements in ethanol production are being researched as water usage and supply are becoming growing issues in many APEC economies. Methods include utilizing alternative heat transfer mediums, such as forced-air fans for cooling instead of cooling water
- Cellulosic ethanol from biochemical processes requires the most water with a ratio of 6:1 water to ethanol. Dry mill ethanol requires a ration of water to ethanol of somewhere between 3:1 and 4:1 and cellulosic ethanol via thermochemical routes water to ethanol ratio averages out at around 1.9:1

- Most APEC member economies fall in regions that do not have a problem with water resources. Member economies such as Peru and Viet Nam have physical water resources but lack the financial capability to develop infrastructure to properly distribute the water supply. Some areas of northern China and mid-west US have limited water supplies
- Overall, however, APEC member economies are in a good position in terms of actual water supply resource based on a very macro economy view

1.4 FEEDSTOCKS

Traditional feedstocks for bio-refinery technologies such as corn and sugar cane for ethanol, and soy and palm oils for biodiesel production are now finding company in a variety of new feedstocks for bio-refineries. These include crops not traditionally grown as energy crops, plants not traditionally cultivated, as well as novel uses of materials previously regarded as waste. Non-traditional energy crops include sorghum, cassava, jatropha, and algae amongst others. Materials previously regarded as wastes include cellulosic biomass, municipal solid waste (MSW), and Publicly Owned Treatment Works (POTW) sludge amongst others. In recent years, there has been an increase in interest about non-food competing energy crops. In order to be considered non-food competing, a crop should be non-edible and should not compete for land and resources with food crops. This has significantly bolstered investment and research into conversion of feedstocks previously viewed as waste (most notably cellulosic biomass) as well as jatropha and algae.

Key findings in regards to feedstock for biofuels production include:

- Though corn and sugarcane are still the predominant feedstocks for ethanol production as soy and palm oils are for the biodiesel industry, in the coming decades, this may not be the case. These food feedstocks may be replaced in the future with non-food competing feedstocks
- Non-food competing feedstocks are being sought and developed throughout the world and are in high demand as some economies will only approve biofuels projects that do not compete with food
- Many novel feedstocks for biofuel production are being investigated and used as alternatives to the traditional corn and sugarcane for ethanol and soy and palm oils for biodiesel
  - Key novel feedstocks being pursued for ethanol production include cassava, sorghum, waste cellulosics, and energy crops grown for cellulosic biomass such as misanthicus and switchgrass
  - Key novel feedstocks being pursued for biodiesel production include jatropha, algae, and waste oils
- Jatropha is being widely pursued around the world and is receiving much attention. This has led it to be poised to become a major feedstock to the global biodiesel industry
- Due to the sheer amount of resources available, research into waste cellulosics conversion may also create a paradigm shift when these technologies become commercially available

- Advances in feedstock development are being driven by sustainability, the food vs. fuel debate, land use, and climate change
- Though not commercially viable yet, it is expected should some of these feedstocks become commercially viable they will revolutionize the global biofuels market, and the global biofuels industry as a whole
- Advances in yield, disease resistance, and growth requirements are being researched in order to decrease farming costs and increase revenues

1.5 CO-PRODUCTS

Co-products of biofuel production are an important part of biofuel production. The co-products can be sold to a variety of markets and in some cases have rendered traditional methods of production not as cost effective. Co-products often serve a vital role in the economic success of biofuels but they do not come without challenges of their own.

Key findings in regards to co-products of biofuels production include:

- Biofuel co-products can be sold for a variety of end uses including:
  - Glycerin as a substitute ingredient for personal care products
  - DDGS as cattle feed
  - Syngas as a feedstock for chemical production
  - Carbon dioxide as a method of food preservation
  - Biochar as a fertilizer to enrich carbon content in soil
- Despite their many end uses, biofuel co-products run the risk of being oversupplied to their markets with increased biofuel production
- Without an end market to sell to, co-products can become more energy intensive and expensive to dispose of
- Concerns of this co-product supply/demand balance are realized and efforts are being made to ensure market demand for these co-products

1.6 BIO-REFINERY WORKSHOP

More than 90 biofuels scientists and engineers from 12 APEC member economies, representing academia, industry, and government agencies, gathered in Chinese Taipei to discuss the bio-refinery technologies. The substantial interest in this workshop was to articulate the suggested biofuel trade and the critical role that chemistry, chemical catalysts, thermal processing, and engineering play in the conversion of lingo-cellulosic biomass into biofuels, including “green” boiler fuel, gasoline, diesel, and jet fuel made from bio-refinery processes.

Key findings in regards to bio-refinery workshop include:

- Availability of non-food feedstocks and cost-effective cultivation system should be studied for bio-refinery technologies.
- Jatropha is a promising feedstock. However, there are many jatropha species and it is important to choose the right species and then to isolate it to prevent contamination,

which can have the effect of changing the species. Although jatropha can grow in arid regions, water is very helpful for the yield. India and China are doing a lot of research concerning.

- Ethanol from corn requires large amounts of water for irrigation. In the US the corn-ethanol plants have reduced water use from 6: 1 to 3: 1. Bio-fuels produced from bio-refinery technologies can further reduce the water requirement by moving from corn to cellulosic crops that require less water.
- There is still a great deal of studies required on the bio-refinery technologies. Cost-effective bio-refinery processes and products should be studied and evaluated; however, the technologies used should consume energy efficiently and generates no additional environmental impact.
- Biofuels can be produced sustainably via fast pyrolysis technology for the application of boiler. After catalytic upgrading, biofuels can be further converted into “green” gasoline, diesel, and jet fuel.
- To reduce bio-hydrogen cost from fermentation, it is not only to reduce the cost of hydrogen production but it is also essential to reduce the cost of wastewater treatment in order to make bio-hydrogen commercially viable.
- Distribution, retailing and vehicle compatibility of biofuels from bio-refinery processes should be evaluated.
- Life Cycle Analysis is needed to measure the opportunity for bio-refinery technologies, although it does depend on the assumptions made and the allocation of co-products. It is the trend in the US and globally.

1.7 RECOMMENDATIONS

Many APEC economies, especially China, Thailand and Viet Nam, have sufficient amounts cellulosic biomass and non-edible crop feedstocks. Therefore APEC economies should continue to focus on these feedstocks for biorefinery application. In addition, FOG feedstocks have potential to be a stable feedstock for biorefineries if APEC economies can efficiently gather this feedstock for processing. China, Indonesia, Malaysia, and the United States in particular have large resources of FOG available.

With respect to biorefinery technologies, fermentation technologies based on food crops such as corn and sugarcane are well established. However, these feedstocks garner controversy as their use as biorefinery feedstocks competes with food supply. As such, focus on non-edible crop and cellulosic biomass based technologies will continue to receive the most attention and development. APEC economies should therefore focus on the development and application of these non-food based technologies.

Biomass pyrolysis currently pursued in Canada, China and Malaysia can also be easily adopted in other APEC economies if similar feedstocks are available. In addition, Singapore’s NExBTL technology is also a worthwhile consideration for other APEC economies. Gasification and FCC cracking are well established technologies in the petroleum-based industries and can be further developed and utilized for biorefinery applications using the feedstocks covered in this study.

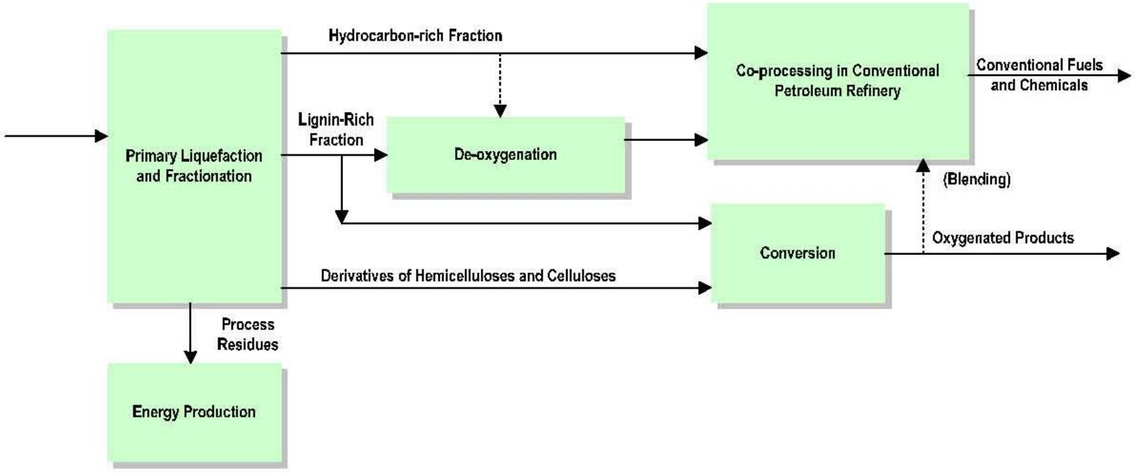
Government incentives and supports are needed for bio-refinery technologies, biofuels production and trade in the APEC region. There is a danger when governments intervene with incentives and mandates, but the reality is that government has its own reasons for wanting to drive alternative fuels and so they need to encourage them.

2.1 INTRODUCTION

Nexant was contracted by the Industrial Technology Research Institute to prepare an informational report outlining current and developing bio-refinery technologies, feedstocks and co-products. This report includes the technical and commercial status of the current leading biofuels such as corn ethanol in the United States, sugarcane ethanol in Brazil, and fatty acid methyl ester (FAME) biodiesel. It also includes emerging "next generation" bio-refinery technologies and types.

The notion of a bio-refinery is comparable to current petroleum refineries where various fuels and products are created from petroleum. The petroleum refinery takes crude oil and fractionates all of the prospective molecular feedstocks for additional processing and blending to generate many different fossil fuel based products. Figure 2.1 shows a generalized process flow diagram of this bio-refining concept. The bio-refinery facility incorporates biomass conversion equipment and processes to generate fuels, power, and chemicals from a biomass feedstock. The facility is able to utilize and maximize the value of the different components in the biomass feedstocks and intermediates. The figure demonstrates how biomass conversion technologies can be integrated into traditional petroleum based refinieries and thus creating a bio-refinery.

Figure 2.1 Overall Bio-refining Concept



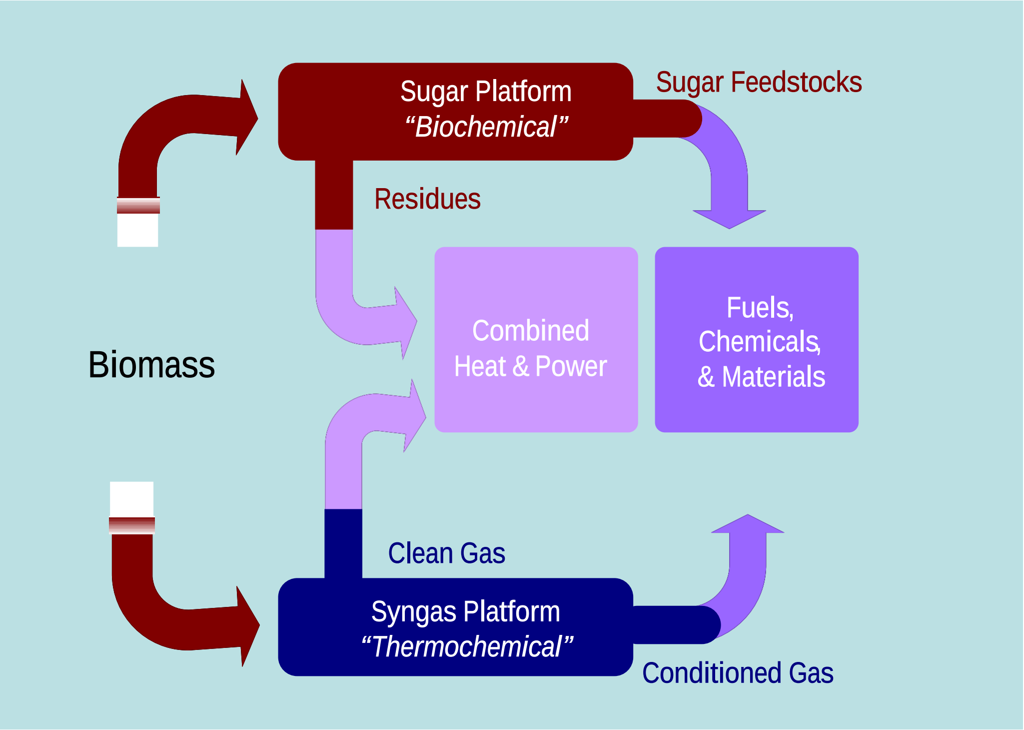
Source: Yrjo Solantausta, 14.3.2006, VTT

Integrated bio-refineries apply many different arrangements of feedstocks and conversion technologies to make various products, with an emphasis on generating biofuels. Some of the side products might include chemicals (or other materials), heat and power. A few of the renewable feedstocks used in the integrated bio-refineries could be grains, such as corn, wheat sorghum and barley, energy crops like switchgrass, miscanthus and willow, and agricultural, forest and industrial residues such as bagasse, stover, straws, sawdust and paper mill waste.

There are a variety of bio-refinery concepts in the research and development stage. The concept of "Whole Crop Bio-refinery" utilizes raw materials such as cereals or corn. The "Green Bio-refinery" is able to process materials with reasonably high water content, like green grass, clover, or immature cereals. The "Lignocellulose Feedstock Bio-refinery" makes use of nature-dry raw materials with high cellulose content, such as straw, wood, and paper waste.

The bio-refinery concept, developed by the National Renewable Energy Laboratory (NREL), breaks up the facility into two different "platforms" in order to get the most out of the product line-ups. The platforms split bio-refinery technologies into two categories, Biochemical and Thermochemical. Figure 2.2 displays NREL's two category bio-refinery concept. Nexant has adopted this method of categorization for bio-refinery technologies and has such organized the following report in this manner.

Figure 2.2 NREL Bio-refinery Concept



Source: NREL

The basis for the biochemical platform is the biochemical conversion processes which concentrate on the fermentation of sugars that are taken from the biomass feedstocks. This platform ferments the carbohydrate content of biomass into sugars that can then be processed to make fuels, chemicals, and other materials. The foundation of the thermochemical platform is the thermochemical conversion processes that center on the gasification of biomass feedstock and the by-products from the conversion processes. The thermochemical process uses pyrolysis or gasification to process the biomass feedstock to generate a hydrogen rich synthesis gas that can then be utilized in various chemical processes.

A bio-refinery has the ability to create one or more low volume, but high value, chemical products and a low value, but high volume liquid transportation fuel. At the same time, it can also make electricity and process heat for its own use and sell a portion of the electricity in some instances. High value products boost profitability for the facility and the fuels produced in bulk volumes would help meet the national energy needs of the economy. The power generated within the bio-refinery will reduce energy costs and help lessen the emissions of greenhouse gases.

Integrated bio-refineries have many benefits because of the diverse feedstocks used and products produced. Currently, bio-refineries have a number of different levels of integration which increases its sustainability, economically and for the environment. A few bio-refinery concepts only generate ethanol or biodiesel while others fully integrate livestock farming or heat and power and other bio-based products. A number of these refineries are self-sustaining with respect to energy consumption.

Archer Daniels Midland Company (ADM) is one of the world's largest grain processors and biofuels manufacturers around the world. The company turns corn, oilseeds, wheat, and cocoa into various products for food, animal feed, chemical and energy uses at their more than 240 processing plants. They represent one end of the bio-refinery spectrum where they use all their raw materials for some kind of purpose at their plants, whether it is for ethanol production or producing food and industrials. ADM is an innovative company trying to increase their crop and cropland productivity, develop better feedstocks for food and fuel, and improve conversion processes and to create new and improved products. Their feedstocks vary from soy protein meal, corn gluten meal to lysine, threonine and other feed ingredients. The products produced by ADM range from food, such as vegetable oil, sweeteners, and flour, to ethanol and biodiesel fuel and industrials like lactic acid, starch and biodegradable plastic.

This report is organized by separating the technologies based on the type of process, such as Fermentation and Thermochemical. The typical Biogasoline and Biodiesel categorization is not as applicable here as some platforms, such as gasification, can be used to make substitutes for gasoline, diesel or jet fuel and not just either/or.

In order to give a complete picture of the status of bio-refinery technologies, challenges and drivers are discussed in the sections below.

2.2 BIO-REFINERY ISSUES AND DRIVERS

2.2.1 Liquid Biofuels Issues

Liquid biofuels are the main focus of bio-refinery production and are the main driving force in bio-refinery technology development. As such it is appropriate to discuss the challenges facing liquid biofuels in today's market.

"Peak oil", climate change, and pollution problems are the key issues related to fossil fuel use that are causing concern across society. Biofuels are perceived as being neutral with respect to the carbon dioxide emissions upon combustion (as contrasted with the fossil carbon released in burning petroleum fuels), since the carbon that is absorbed from the atmosphere to grow a plant is simply released again upon combustion of the plant's biofuel derivatives. This carbon neutrality based on feeds must be netted against any fossil fuel requirements for agriculture, transportation and for manufacturing the fuel. If the systems that support the production of the biomass and the conversion processes as well as transportation also derive their energy needs from biomass or other renewable sources, biofuels can be completely free of greenhouse gas emissions. At least in their present forms of ethanol and biodiesel, liquid biofuels are non-toxic and biodegradable and the emissions and residuals from their manufacturing processes and handling are in general less problematic in terms of human health and environmental risks. Many initiatives are underway to develop and produce biofuels (gasoline, diesel, and jet fuel) that are chemically closer to the hydrocarbon liquid fuels from petroleum sources in use today. While these renewable hydrocarbons and higher alcohols may be more convenient than ethanol and fatty acid esters, they trade off convenience for greater toxicity in most cases.

Many policy makers, industry planners, aware citizens, and the financial community are interested in the potential for substituting biologically-derived fuels for those based on petroleum or natural gas, especially gasoline and diesel motor fuels. The leading motivations for this interest include:

- Increasing oil prices/supply constraints:
  - Consumer cost savings at the pump
  - Overall economic health
- Government policy-related issues:
  - Long term petroleum and gas fuel supply security, which relates to many types of risk (biofuels, which tend to be produced with local agricultural resources in many relatively small facilities, are seen as a kind less vulnerable “distributed generation”)
  - Reducing geopolitical pressures of obtaining imported petroleum and natural gas supplies
  - National balance of payments
  - Reducing carbon dioxide “greenhouse gas” emissions related to climate change
  - Reducing other pollutant emissions associated with supply, processing, and use of liquid fuels
  - Rural development, enhancement of the agricultural sector (e.g., response to farmer lobbies)
  - Sustainable economic development
- Technology developments making biofuels a potentially more feasible and attractive alternative fuel option than others (regional focuses vary), including:
  - Genetically modified crops and biomass energy feedstocks enabling more secure, higher efficiency agriculture
  - Genetically engineered enzymes for fermentation enabling higher conversions to biofuels
  - Bioprocessing and chemical process improvements, creating more optional routes, better matching the technical requirements of motor fuels

Motor fuels present special technical and logistic challenges for fuel substitution. In contrast, for example, there is a wide diversity of feasible alternatives for generating electricity, from coal and natural gas combustion, nuclear fission, hydroelectric and wind power, to photovoltaic and solar thermal energy. Natural gas, gas condensates, fuel oil, petroleum residuals, and waste materials serve most of the total of space heating and industrial fuel needs, and for the latter, a high degree of switching capability is already in place.

In contrast to these energy systems, motor fuels have a very specific range of properties required to serve the existing vehicle fleet and to be handled in the existing distribution and refueling infrastructure. The existing investment in motor fuels refining and a vast distribution infrastructure is in the trillions of dollars in the United States and globally. The vehicle fleet would take decades to be substantially turned over if we were to substantially replace petroleum fuels with alternative fuels that have very different properties and characteristics, such as CNG, electricity, or hydrogen. It is therefore desirable to produce biofuels that blend well with conventional liquid fuels or are "drop-in" substitutes for them. Otherwise, society faces the dilemma– who will buy alternative fuel vehicles without the stations to supply them, and conversely, who will build the distribution infrastructure and stations without vehicles to supply?

Agricultural feeds are different from hydrocarbons fed to petroleum refineries and products from natural gas processing. The value chains for the bio-feeds have major impacts on, and market dynamics entwined with sectors other than fuels. In contrast, non-fuel products, except for some chemical feedstocks, have relatively less impact on the economics of petroleum refining.

The complex value chains for bioethanol, biodiesel, and next generation biofuels, including feed and co-product issues, etc. are discussed in Section 4, Feedstocks.

Many look forward within the next few years to changes in these patterns, including producing ethanol based on fermentation of sugars derived from abundant cellulosic resources, while for biodiesel, jatropha, algae, and other non-food sources are looked to for better sustainability and social responsibility. Also, in the near term, these as well as more conventional oils and fats may be fed directly to petroleum refining hydrogenation processes, with the resulting diesel-range hydrocarbons handled together with those from petroleum. Such approaches are more favored by the refiners and marketers that have to ultimately handle most liquid biofuels.

2.2.2 Bio-refinery Technology

"Bio-refinery technology", for both conventional as well as next generation technologies, represents a number of diverse aspects and developmental challenges along the product value chains. These are primarily categorized as follows:

- Plant Biotech (crop genetics)
    - Improving land yields of existing crops for sugars, starches, oils, and/or biomass, with less agronomic inputs, better quality products
    - Developing new crops for higher yields or improved types of sugars, starches, oils, and/or biomass (e.g., energy cane, jatropha, etc.)

- Microbial biotech

  - Developing better, more cheaply produced grain and cellulosic biomass liquefaction/saccharification enzymes for exogenous use or microbes for these tasks, and better fermentation microbes for biofuels production, such as for ethanol or butanol fermentations, especially for utilizing C_5 sugars
  - Microbial routes to other alcohols and other biofuels (especially bio-hydrocarbons) from sugar or cellulosic substrates
  - Fermentation of carbon monoxide (bio-syngas) to alcohols, etc.
  - Improved microalgae strains to overcome conventional physical limitations and challenges

- Bioprocess improvements – other than biotech
  - Faster, cheaper, more compact physical/chemical pretreatments
  - Lignin separation and use
  - More efficient distillation and dehydration (e.g., for ethanol)
  - Improved fatty acid esterification (e.g., by heterogeneous catalysts)
  - Recovery of biodiesel co-product glycerin
  - Less production of by-products and residues
  - Biomass energy supply and recovery (e.g., by biodigestion, gasification, etc.)
  - Improved growing regimes and cell concentration and oil separation techniques for microalgae systems

- Chemical process improvements – applications of conventional thermo-chemical and catalytic processing to biomaterials
  - Partial oxidation gasification of biomass (pyrolysis)
  - Hydrocracking and isomerization of natural fats, oils, and greases to fuel hydrocarbons
  - Steam catalytic cracking of biomass, oils, and/or alcohols using FCC-like processing
  - Fischer-Tropsch catalysis of biosyngas to make gasoline or diesel fractions, higher alcohols, etc.

- Novel departures from the all of the above, including to date:
  - Catalytic conversion of sugars in solution to hydrocarbons or hydrogen
  - Fermenting sugars to lipids using algae species (non-photosynthetic)
  - Fermenting sugars directly to hydrocarbons for conversion to gasoline, diesel, jet fuel, and/or substitutes for common petrochemicals
  - Derivatization of chemicals or fuels from alcohols (e.g., methanol-to-gasoline, ethanol-to-gasoline, ethylene, butadiene, *n*-butanol, etc.)
  - Algae production of ethanol
  - Fermentation of sugars to acids, followed by conversion to alcohols

- Distribution and use of biofuels in existing systems

- Disposition of bio-based chemical products as they replace their petroleum based counterparts

2.2.3 Feedstock Challenges Have Emerged

Challenging biofuels development, the “food versus fuel” debate has escalated with both the public and among public policy-makers. Biofuels in the popular press are being blamed for high food prices as well as hunger in developing economies. As a result, China and other economies have banned grain and certain land use for biofuels. Germany and other counties are back peddling on biofuel goals. Critiques have also been published of biofuels as having a poor “carbon footprint” and being uneconomic without subsidies. Each of the above issues is as yet unresolved, with much of the information published being based on incomplete analysis or in some cases politically motivated.

Biofuels production based on food commodities or even using agricultural lands is falling out of favor with many, with the obvious exception of corn and sugarcane industry producers and stakeholders. Concerns are being raised over CO_2 emissions from agricultural fuel and fertilizer use, N_2O greenhouse gas emissions from fertilizers and tilling, and ethanol and biodiesel processing energy use. Additional agricultural/environmental issues have been raised over land use, soil depletion, water use, and deforestation. Because these concerns have received so much attention, the focus of much industry activity has shifted to development of feedstocks based on cellulosic biomass and non-food lipid sources such as jatropha and algae. Others worry that these solutions are being over-hyped and are not as feasible as claimed by their proponents.

However, in the United States, Brazil, and elsewhere, society and governments continue to look tentatively to biofuels as an alternative to petroleum. In the United States, the Energy Independence and Security Act that was enacted in December 2007 increases requirements for total use of renewable fuel (the Renewable Fuel Standard, or RFS) to 36 billion gallons by 2022. As in the 2005 Law, a target trajectory of demand buildup is defined. The new 2007-defined RFS is summarized in Table 2.1, along with the required contributions of advanced and cellulosic biofuels and biodiesel during the period. Other regions that are global leaders in biofuels are Brazil, as stated before, and Western Europe. Key economies in Asia, in particular China and India, are emerging leaders.

Table 2.1 2007 Energy Act RFS-Mandated Schedule of Use

Renewable Fuels Required Billions of Gallons				
Year	Total	Advanced Biofuels Contribution	Cellulosic Biofuels Contribution	Biodiesel Contribution
2008	9.0	ns	ns	ns
2009	11.1	0.6	ns	0.5
2010	12.95	0.95	0.1	0.65
2012	15.2	2.0	0.5	1.0
2015	20.5	5.5	3.0	ns
2018	26.0	11.0	7.0	ns
2020	30.0	15.0	10.0	ns
2022	36.0	21.0	16.0	ns

ns= not specified in the Act

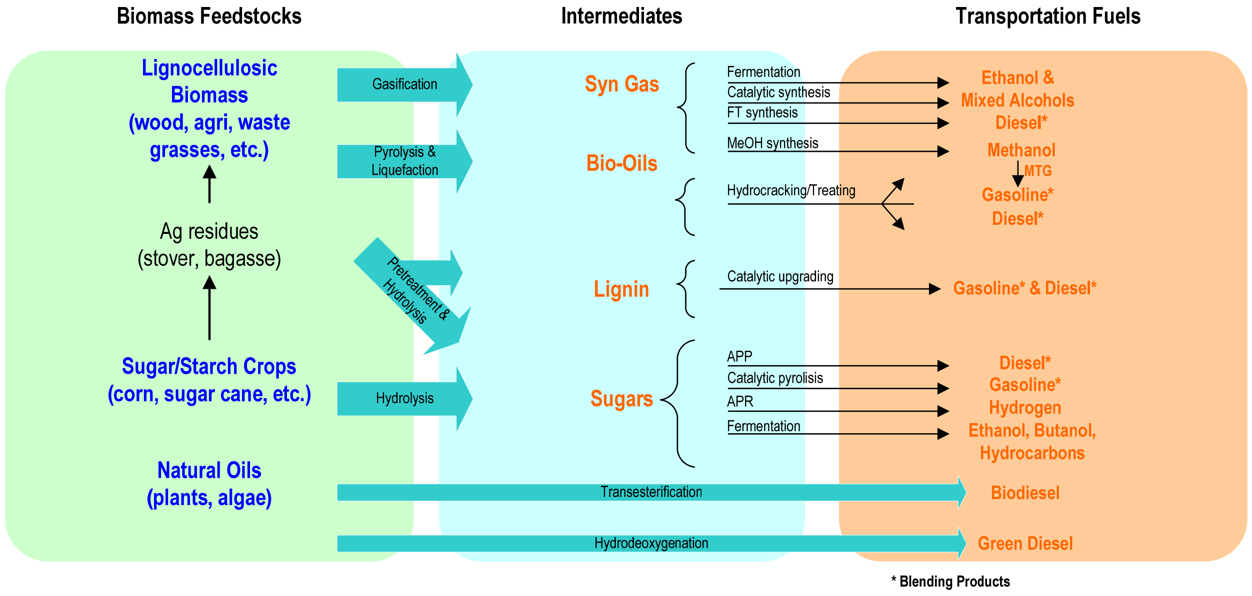
Despite concerns for food-versus-fuel, at least in the United States with a new biofuels-friendly Obama Administration, it is not expected that the drivers for cellulosic and advanced biofuels will be significantly weakened, or even for corn ethanol.

3.1 OVERVIEW

Bio-refineries employ the use of biomass conversion technology to produce fuels, chemicals, heat and power traditionally generated by petroleum and fossil fuels. The most significant products produced from bio-refineries are biofuels. As the world tries to lower its dependence on petroleum, bio-refinery technologies are taking the lead in ushering in a new era of bio-based products.

There are a number of technologies available or in the developmental stage that produce different types of biofuels, from ethanol to butanol to ester-based biodiesel to hydrocarbons. Ethanol is a good fuel to supplement or substitute for petro-gasoline; however, it has a number of issues ranging from performance characteristics to production costs. It is the only major biologically-derived fuel being used as a substitute for petroleum gasoline in the world today, but there is concern over global limits on the availability of feedstocks. Nexant and many other experts foresee the commercialization of several second generation biofuel products and processes that augment or supplant grain and sugar ethanol as a substitute for gasoline over the next decade, and/or utilize lipids other than by transesterification, alongside the development of third generation biofuels. Figure 3.1 displays the different biofuel options in various technologies that are available beyond the ethanol fermentation route.

Figure 3.1 Transportation Biofuels Process Options



Source: National Renewable Energy Laboratory (NREL)

The different routes used, based on the type of biomass feedstock being utilized, include direct conversion processes such as the extraction of vegetable oils followed by esterification (biodiesel), fermentation of sugar-rich crops (ethanol), pyrolysis of wood (pyrolysis oil-derived diesel equivalent) or the production of liquid biofuels (methanol, ethanol, mixed higher alcohols, Fischer Tropsch liquids, etc.) from synthesis gas made by gasification of biomass. Table 3.1 shows the main biomass properties for bioconversion and thermochemical conversion to liquid biofuels. The numbers represent the importance/relevance of the particular property to the process with 1 representing the most important/relevant and 3 representing the least important/relevant.

Table 3.1 Main Biomass Properties for Bioconversion and Thermochemical Conversion to Liquid Biofuels

	Bioconversion		Thermochemical
Property	Acid Hydrolysis and Fermentation	Pretreatment followed by Enzymatic Hydrolysis and Fermentation	Gasification Followed by Fischer-Tropsch Synthesis
Quantity of Sugars	1	1	3
Structure and Quantity of Ligin	1	1	3
Cellulose Crystallinity	2	1	3
Bulk Density	3	2	1
Particle Size	2	2	2
Moisture Content	3	3	1
Extractive Content	3	3	3
Nitrogen Content	3	3	2
Sulfur Content	3	3	2
Other Organics	2	2	2
Calorific Value	3	3	2

Source: Clayton, David, Ralf Moller, Marcel Toonen, Jan van Beilen and Elma Salentijn. Outputs from the EPOBIO project, April 2007

This section details the current technologies and potential second and third generation approaches, including:

- Fermentation of sugar, starch, grain and lignocellulosic biomass substrates at likely locations in the United States, Western Europe, Brazil, China, India, and Thailand, using the most relevant feedstocks for each venue
- Various leading options for pretreatment and hydrolysis of lignocellulosic biomass to produce fermentable sugars, plus means of integrating these steps and fermentation with on-site energy production

- An alternative alcohol, *n*-butanol, made by established and emerging fermentation-based routes
- Hydrocarbons generated by fermentation processes
- Fischer-Tropsch gasoline-range fuels made from biosyngas
- Methanol made by pyrolysis and by catalytically converting biosyngas
- Higher alcohol mixtures made in various catalytic processes from biosyngas
- Technologies for ethanol derivatives – hydrocarbons and other biofuels made from ethanol, including Sangi HAP gasoline, Mobil MTG/ETG and ethylene
- Other approaches, such as the ZeaChem Indirect Ethanol Process that starts with bacterial fermentation of carbohydrate substrates to make acetic acid, followed by esterification, followed by hydrogenation to ethanol, with recovery and recycle of the alcohol, and generation of the needed hydrogen from biomass

3.2 FERMENTATION

3.2.1 Starchy Feedstocks – Overview

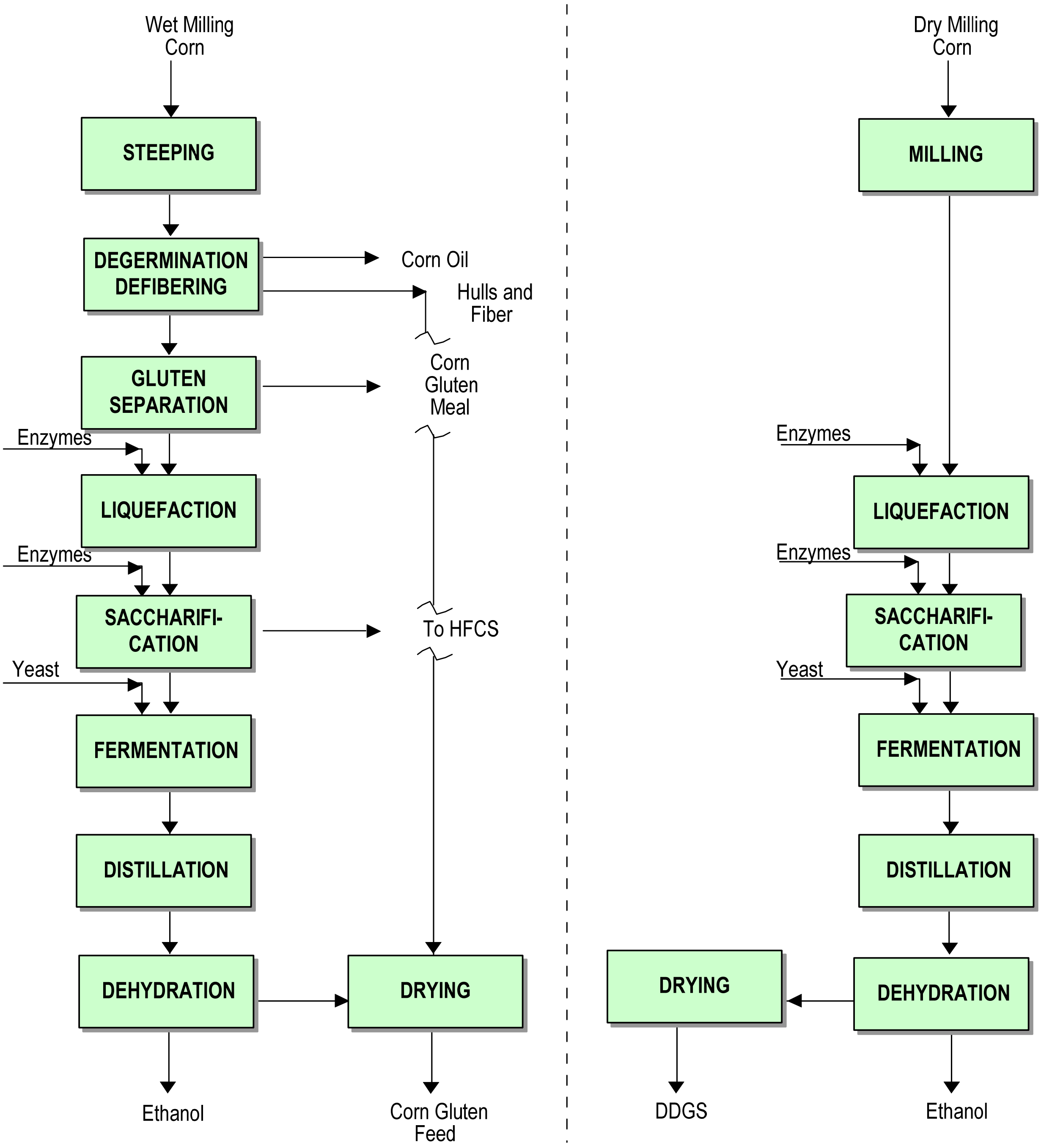
A variety of starchy materials can be used for fermentation to ethanol. The selection of raw materials often depends on the availability for large scale production. Corn, wheat, sorghum (milo), and potatoes are the most common raw materials in North America and Europe, whereas cassava and sweet potatoes (yams) are more important in tropical and sub-tropical regions. Sweet sorghum is a variety grown in both subtropical and temperate zones for its sugar juice and not for its grain, and is now being developed for fuel ethanol production. Rice is not being used for fuel ethanol production anywhere.

3.2.2 Corn to Ethanol

Corn is fermented to ethanol in either wet corn milling or dry corn milling processes. The former is also known as a bio-refinery because it produces a number of diverse food and industrial products in the same facility, and can be designed to switch with seasonal changes in market demand between high fructose corn syrup (HFCS) production and ethanol, similar to the manner in which many sugarcane ethanol plants are operated with respect to crystal sugar production. However, most of the ethanol production in North America from corn is by dry milling. The processes for grain sorghum, wheat, and other grains are very similar.

The major differences in unit operations between dry milling and wet milling are the initial treatment of corn (milling versus steeping) and the production of by-product of dried distiller grains with solubles (DDGS) vs optional HFCS and corn gluten feed. Each process has inherent advantages and disadvantages. Figure 3.2 compares the block flow diagrams of wet milling and dry milling. The details of both dry milling and wet milling are described in the following sections.

Figure 3.2 Wet Milling versus Dry Milling



The following presents ethanol production by dry milling of corn, with some references to wet corn milling as well.

3.2.2.1 Corn Dry Milling

The whole-kernel dry milling process is the simplest of the processes considered, and is usually the one recommended for new entrants into the market. The advantages of dry milling over wet milling are that the process is simpler to operate, and dry milling has lower capital and operating costs than wet milling.

While dry milling produces a slate of by-products that are overall less valuable than the wet milling process, it avoids the need for swing production and syrup integration, therefore avoiding the need of the entrant to compete in the corn syrup and sweetener market.

Table 3.2 provides a typical analysis of the corn used in milling operations.

Table 3.2 Typical Corn Analysis

(Weight Percent)

Component	Composition
Ash	1
Fat	3.7
Fiber	1.9
Nonfermentable elements (NFE)	8.6
Protein	8.4
Starch	60.8
Water	15.6
Total	100

The following figures graphically illustrate the operation of the whole-kernel dry milling process:

Figure 3.3	Corn Receiving, Storage, and Cleaning
Figure 3.4	Corn Milling and Hydrolysis
Figure 3.5	Saccharification
Figure 3.6	Fermentation
Figure 3.7	Ethanol Beer Still
Figure 3.8	Ethanol Rectifier and Dehydration
Figure 3.9	Distiller's Dried Grains and Solubles (DDGS) Production
Figure 3.10	Ethanol Pasteurization and Vent Recovery

Figure 3.3 Corn Receiving Storage and Milling Whole Kernel Milling

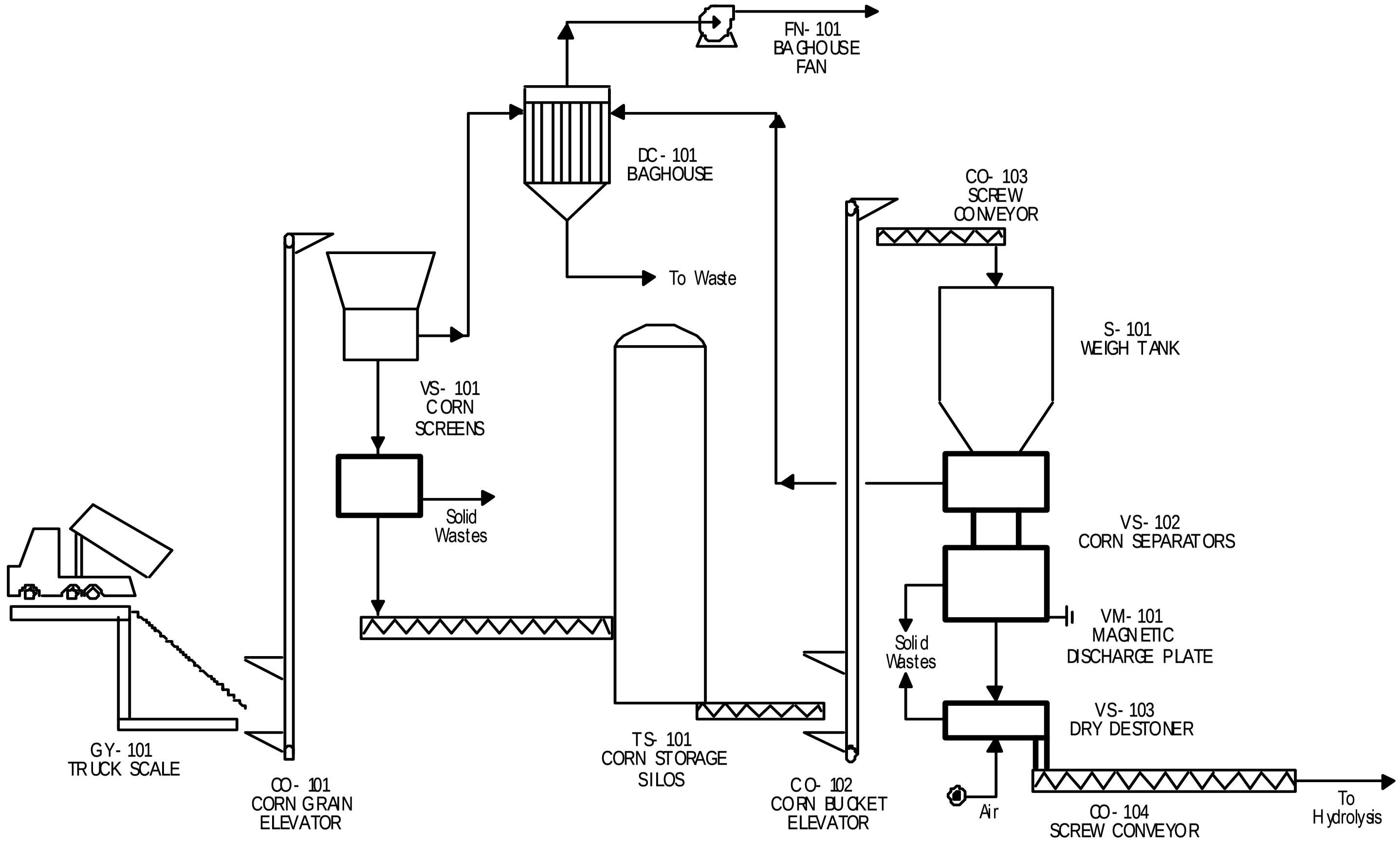


Figure 3.4 Milling and Hydrolysis Whole Kernel Milling

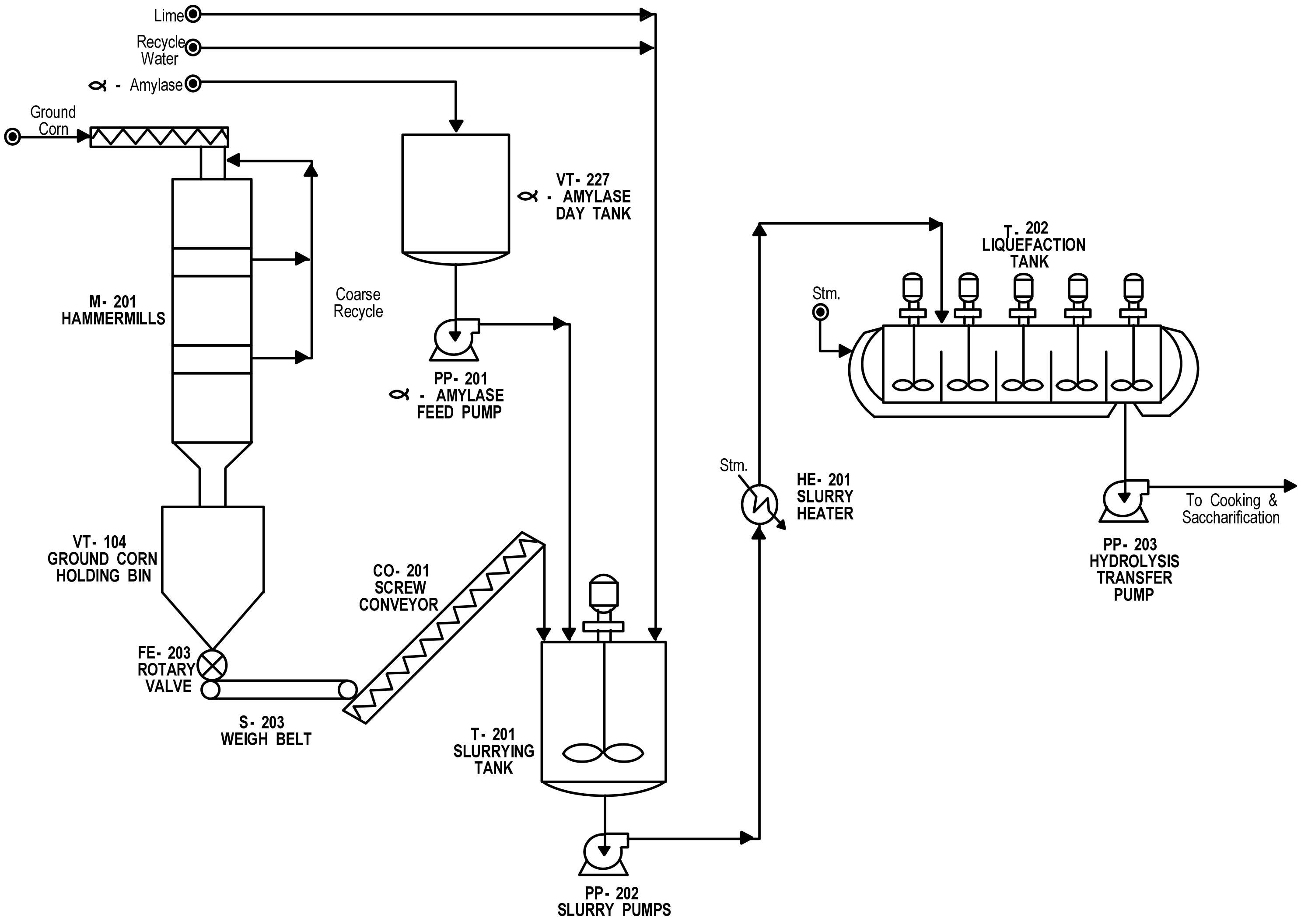


Figure 3.5 Saccharification Whole Kernel Milling

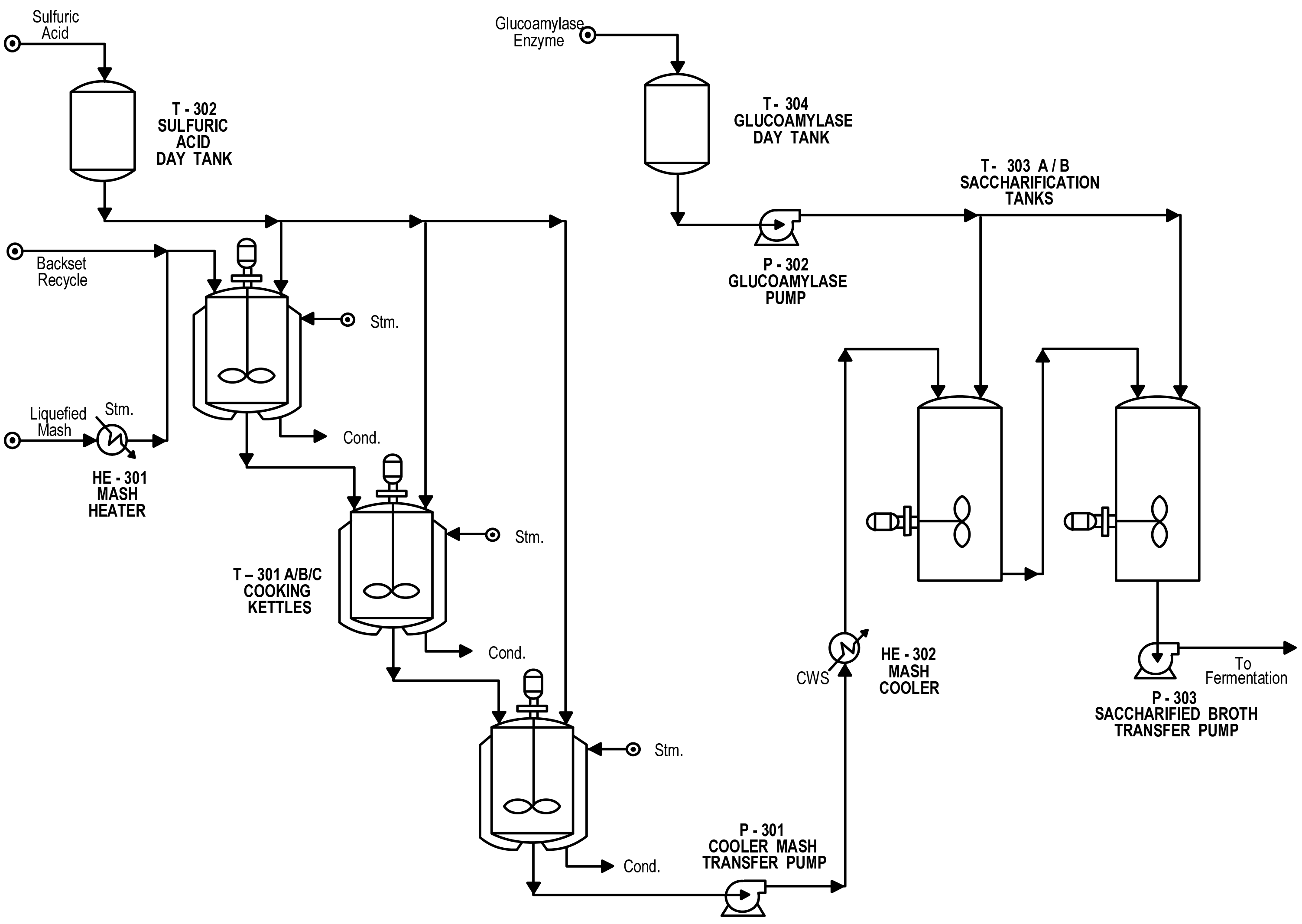


Figure 3.6 Fermentation Whole Kernel Milling

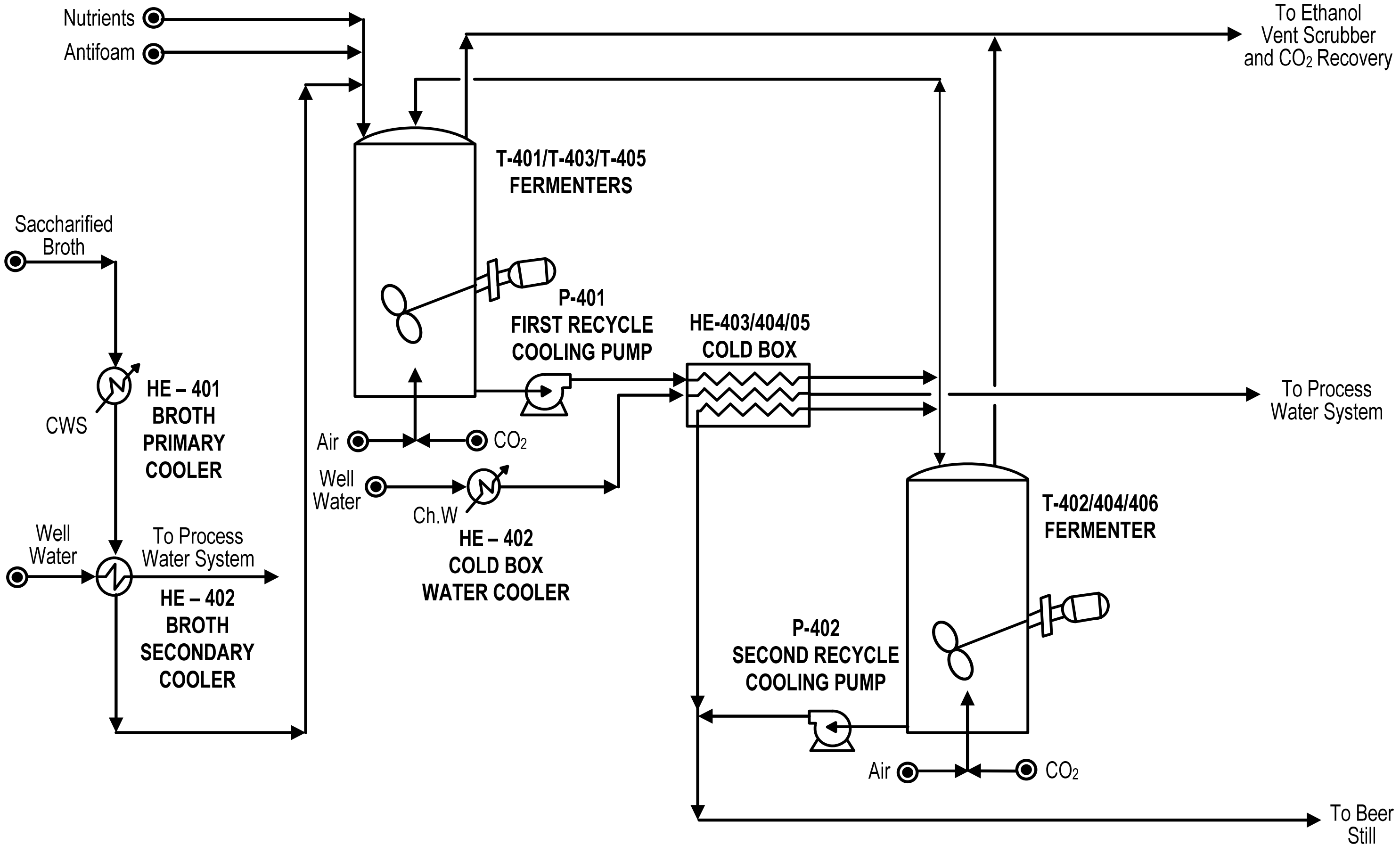


Figure 3.7 Beer Still Corn Dry Milling

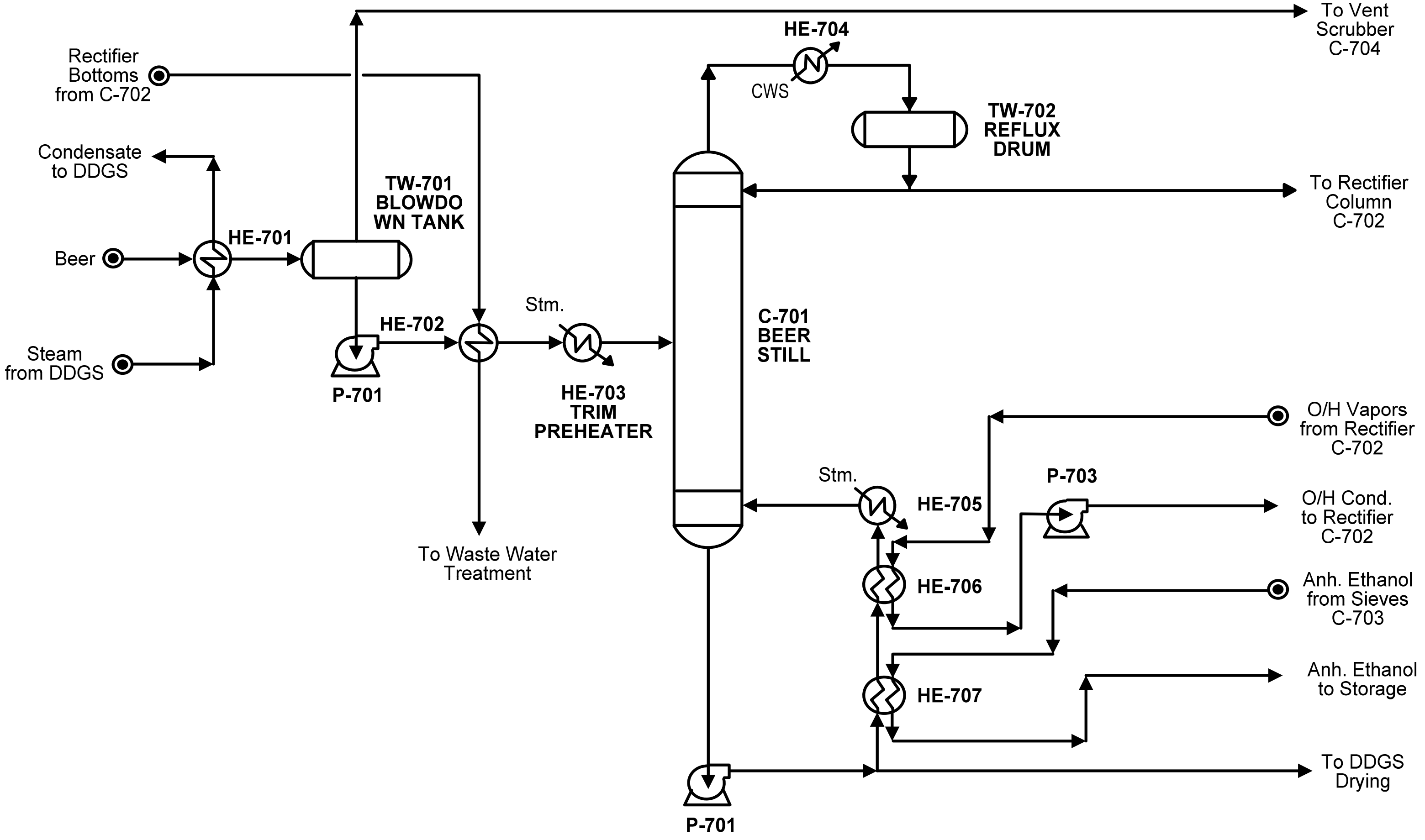


Figure 3.8 Rectifier and Dehydration Corn Dry Milling

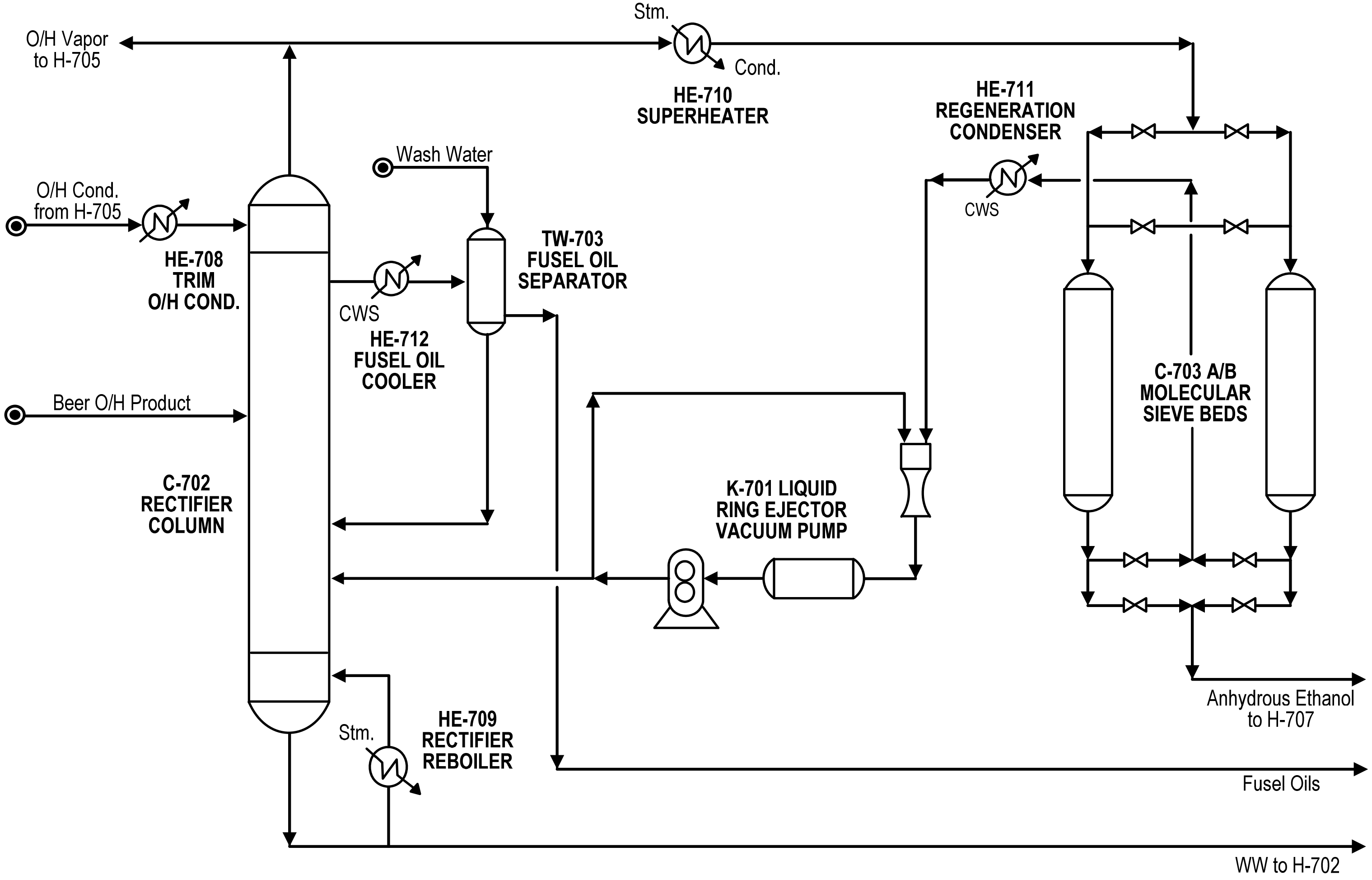


Figure 3.9 DDGS Drying Whole Kernel Milling

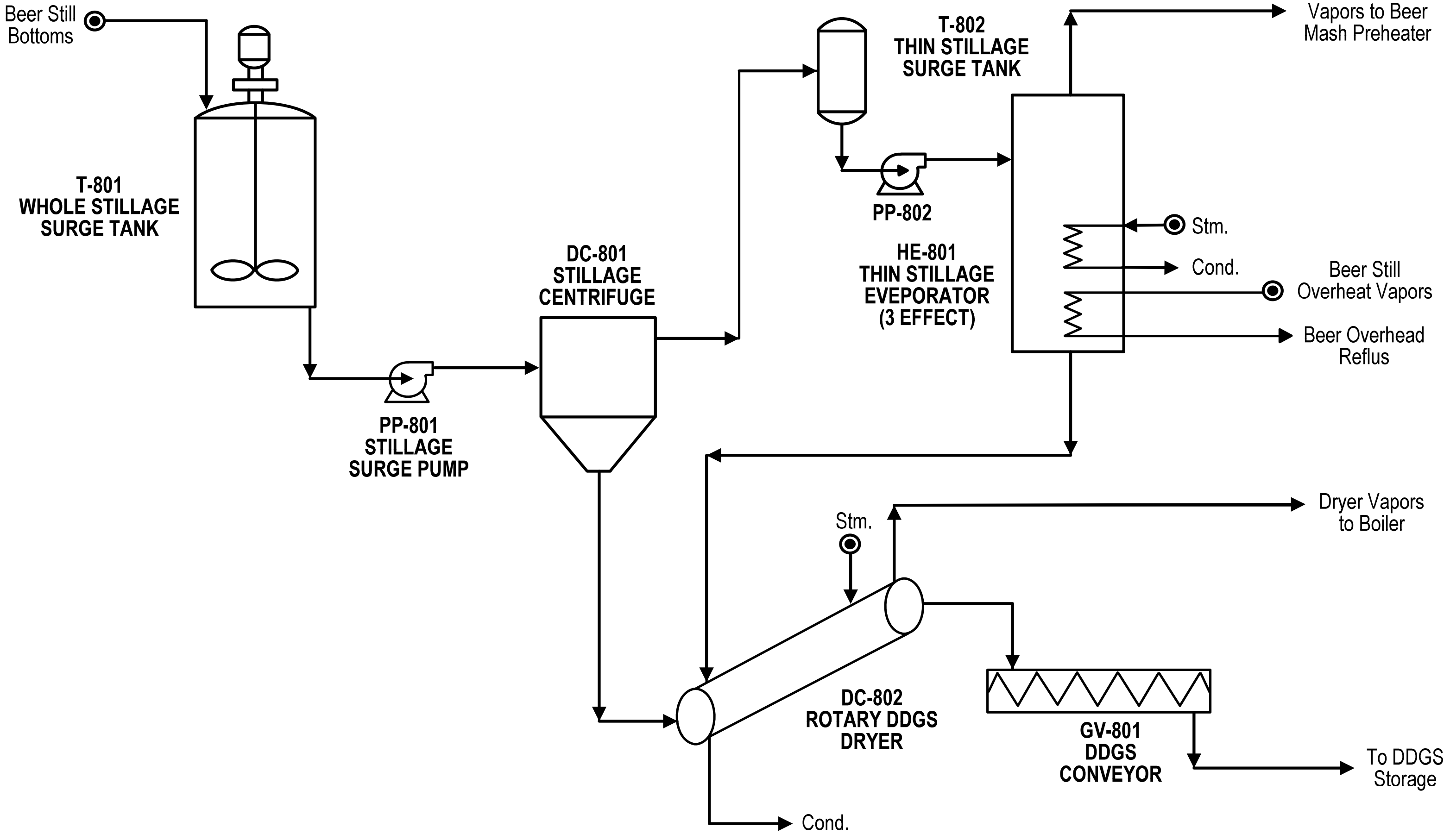
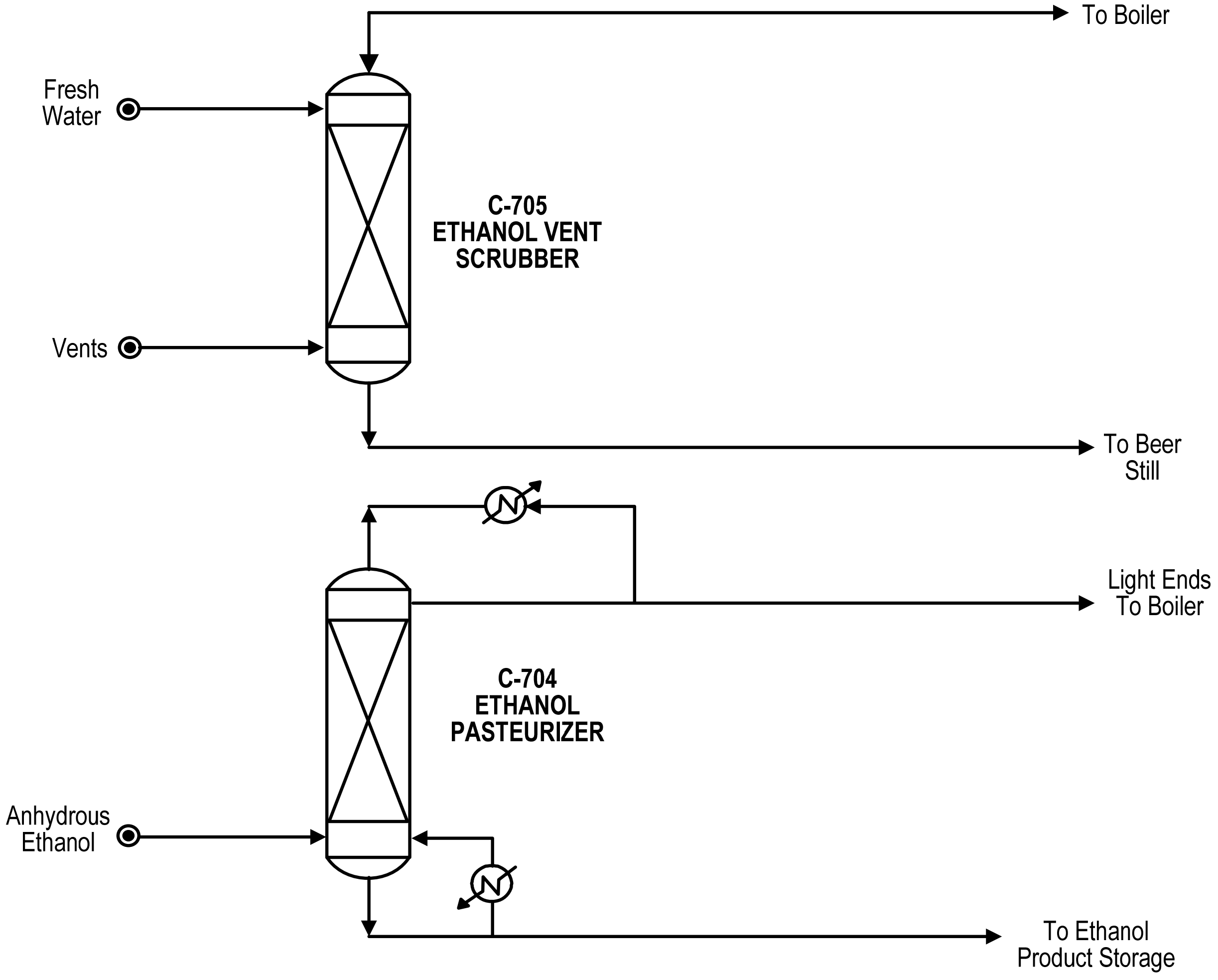


Figure 3.10 Ethanol Pasteurization and Vent Recovery Whole Kernel Milling



The process description is based on information supplied by the Delta-T Corporation, of Williamsburg, VA. Delta-T has been involved in all aspects of ethanol made by grain fermentation since the 1970s.

Corn Receiving

Shelled corn is received, generally by truck but occasionally by rail. The trucks and/or railcars are weighed on scale Figure 3.3 GY-101 on entering and leaving the compound. The corn is offloaded into a temporary storage pit, where it is tested for quality and moisture content. The corn is then screened to remove debris, remaining pieces of cob, chaff, dirt, and other foreign objects (via Figure 3.3 VS-101 and VM-101). Corn is received five days per week, eight hours per day, and typically 320 days per year. Ten days corn storage is provided in silos Figure 3.3 TS-101, assuming the supplier maintains seasonal storage space for the corn to maintain off-season supplies. Table 3.3 illustrates the safe storage life of No. 2 yellow corn, 15.5 percent moisture, stored at various temperatures.

Table 3.3 Safe Corn Storage Life
(Days)

Storage Temperature	Corn Moisture Content (Wet Basis), %			
°F	15	20	25	30
35	1,140	118	42	25
45	725	75	27	16
55	337	35	12.5	7.5
65	207	21.5	7.8	4.6
75	116	12.1	4.3	2.6

Grain is delivered to the plant from the storage silos via bucket elevator Figure 3.3 CO-102 and overhead screw conveyor Figure 3.3 CO-103, which convey the corn from the elevator to weigh tank S-101. Once weighed, the corn is gravity-fed to corn separators Figure 3.3 VS-101A/B for removal of fine and coarse impurities from the corn feed. These separators have a swinging body suspended from a metal frame, which undergo a swinging circular motion over a pair of metal sieve decks. The discharge plate is magnetic to capture any metallic objects that are carried through. From the discharge aspirator, which is between the pair of metal sieve decks, the separated corn gravity flows to the dry destoners Figure 3.3 VS-103 A/B/C/D for stone and pebble removal. The stones are separated by gravity by floating the corn on a bed of air, and allowing the stones and other materials of similar or higher density to fall below. The cleaned corn is then conveyed by screw conveyor Figure 3.3 CO-104 to the mill feed bin Figure 3.4 VT-104. The weigh belt Figure 3.4 S-203 acts as the primary accounting mechanism for the quantity of corn fed to the dry mill portion of the plant. The cleaning operation loses approximately 1 percent of the corn fed from the delivery units.

Milling and Hydrolysis

Hammermills Figure 3.4 M-201 A and B provide the milling action, grinding the corn into fine flour. Any coarse material is recycled back to the mill. A hammermill is a vertical mill consisting of flat metal hammers mounted on a rotating shaft, with the hammers free to swing on a pin. The grains fed from the top of the mill fall downward through the enclosed vertical space, and are smashed by the hammers against a flat, stationary breaker plate. The crushed material falls to a bottom grate, where any particles larger than the grating are recycled to the top of the mill. The mill comprises three such hammer units, placed vertically in series.

The milled material falls into the ground corn holding bin Figure 3.4 VT-104. The ground corn is then fed by a rotary valve Figure 3.4 FE-203 to weigh belt Figure 3.4 S-203. The weighed material is conveyed by screw conveyor Figure 3.4 CO-201 to the slurrying tanks Figure 3.4 T-201. Here, the ground corn is mixed with α-amylase enzyme and recycled water. The slurry is then mixed in the tank for a total retention time of 5 minutes. The mixed slurry is heated by indirect steam contact in the slurry heaters Figure 3.4 HE-201, using 150 pound steam from the boiler units. The steam heats the slurry to 80°C and sends it to the liquefaction tank Figure 3.4 T-202. Lime is added to the liquefaction tank to maintain pH.

The liquefaction tank is a multi-baffled system, with each compartment agitated by a dedicated overhead-mounted agitator. The tank retains the slurry for a total of 1 hour, while the α-amylase enzyme breaks down the starch into soluble simpler starches, glucose, and dextrose units. During liquefaction, additional steam is fed to the liquefaction tank blanket to maintain temperatures at 180°F. Residence time is optimized to reduce the formation of dextrin units (glucose dimers) that are not fermentable by downstream yeasts.

The liquefied material is then transferred by the liquefied mash pump Figure 3.4 PP-203 to the cooking tank, Figure 3.5 T-301.

Glucoamylase enzyme (AMG) catalyzes the hydrolysis of the 1,4-glucosidic and 1,6-glucosidic terminal bonds from the non-reducing ends of the starch to free individual glucose units. AMG is usually added as a cell-free extract from Aspergillus Niger.

As with all catalysts, AMG also catalyzes the condensation of glucose units into maltose and isomaltose. The latter is not fermentable by yeasts used for ethanol production, but is formed at a much slower rate than maltose, which is fermentable. This reverse catalysis sets a limit on the concentration of glucose available in the broth; at dextrose equivalent conversions of greater than 97 percent, the reverse reaction becomes dominant and further conversion of the starch is usually not attainable.

Enzyme concentrations are measured not on a stoichiometric basis but by an activity basis, or activity units. The activity units for each enzyme must be experimentally derived by a rate assay (usually spectrophotometry). Activity units can be converted by determining how many active sites per enzyme are present per weight or volumetric basis (either contained or diluted enzyme).

Various enzymes with different activity-temperature profiles, activity concentrations, and saccharification potentials exist on the market today, allowing a wide variety of conditions for saccharification. This particular design is set for rapid saccharification at moderately low saccharification temperatures in order to minimize the probability of biological activity from contamination.

Cooking and Saccharification

The liquefied product is transferred from the liquefaction tank and heated using the mash heater Figure 3.5 HE-301. The mash heater uses 150-pound steam to raise the mash temperature to 110°C. The hot mash is then sent to the cooking kettles, Figure 3.5 T-301 A, B, C. Sulfuric acid is added to the mash in the first cooker. The sulfuric acid provides the acid hydrolysis needed to break up and loosen any polymeric materials (lignin, cellulose, etc.). This acid action also results in some starch to glucose conversion. The acid-hydrolyzed material has more surface area and higher porosity, which maximizes the conversion efficiency of the glucoamylase enzyme.

The mash flows by gravity to the second and third cookers in series. Total cooking residence time is maintained at 15 minutes to minimize by-product formation. Acid hydrolysis can lead to the formation of undesired products such as methanol and various fusel oils. Each cooker is maintained at 110°C by a steam blanket.

Following the completion of the processes in the last cooker, the mash is transferred via the cooked mash pump Figure 3.5 PP-301, which passes the mash through the mash cooler Figure 3.5 HE-302. The mash cooler uses cooling tower water to cool the mash from 110°C to 60°C, the optimal operating temperature for glucoamylase enzymolysis.

The cooled mash is then sent to the saccharification tanks Figure 3.5 T-303 A/B. The saccharification tanks are also fed with a continuous solution of glucoamylase enzyme. The saccharification tanks are set up as a cascade series, the first feeding the second by gravity flow. The two tanks provide a total saccharification residence time of 2 hours. Agitation to the tanks is provided by three side-mounted agitators. The tanks are made of 316SS.

The saccharified broth, typically converted to a dextrin equivalent of 95, is pumped via the saccharified broth pumps Figure 3.5 P-303 to the fermentation area.

Fermentation

The saccharified starch is pumped from storage tank Figure 3.5 T-303 in a two-step cooler: the primary cooler Figure 3.6 HE-401 uses cooling tower water to cool to 40°C, and the secondary cooler Figure 3.6 HE-402 uses well water at 15°C to cool the diluted slurry to 35°C. The well water is then sent to the process water storage tank. Well water use reduces the need for a chilled water system, which introduces significant additional capital and operating costs. In winter months, well water use would be minimal, since the cooling tower would be able to cool the diluted stream sufficiently. A higher capital cost for the larger exchanger surface area of Figure 3.6 HE-401 is justified by the reduction of the chilled water system.

The saccharified broth is pumped to the cascade set of fermenters. The fermentation occurs in three parallel trains of two tanks each. Each train is designed to ferment 50 percent of the total flow through the fermentation area. The total residence time provided by the equal sized tanks is 20 hours. The tanks are made of 316L stainless steel.

Each tank operates at a steady state condition, with sugar concentration decreasing stepwise and ethanol concentration increasing stepwise from the first to the last tank.

The heat of fermentation, 1.2 MJ per kilogram of ethanol, is removed by the side-stream coolers Figure 3.6 HE-403/404/405. Well water available at 15°C is used as the primary cooling medium. In summer months, the well water is supplanted and/or cooled by a chilled water system.

Oxygen is added to the fermentation broth. Total anaerobic conditions favor yeast growth, not ethanol production, so some oxygen is necessary to promote ethanol production. Air is first filtered then pumped into the draft tube along with the feed broth. Carbon dioxide is recycled from the CO_2 recovery area to provide additional agitation, and to minimize the contamination of carbon dioxide in those plants where the gas is collected and purified for sale.

Carbon dioxide byproduct is separated from the beer in the disengaging section of the reactor. The gas is then pumped through a common header by suction on the scrubber provided by fan Figure 3.3 FN-105 to the gas scrubbing section.

An alternative design for the fermenters is discussed in the next section, which describes the use of either a flocculating yeast tower or simultaneous saccharification and fermentation (SSF), instead of cascade CSTRs (continuous stirred tank reactors).

Distillation

The dilute beer from the fermentation area undergoes a series of preheating steps. First, the beer is preheated against the flash vapors from the distiller's dried grains and solubles (DDGS) drying area in Figure 3.7 HE-701, heating the beer to 65°C. The beer is then flashed in flash tank Figure 3.7 TW-701 to remove any remaining gases and stabilize the column operation. Any vent gases are sent to the fermentation vent scrubber to recover entrained ethanol. The beer is then further preheated to 100°C against the rectifier column bottoms in Figure 3.7 HE-702. The beer still feed trim heater Figure 3.7 HE-703 preheats the beer to a final 110°C prior to the beer still.

The hot, dilute beer enters beer still Figure 3.7 C-701, which operates at a slightly positive pressure of 130 kPa. The column has 60 actual trays. The solids and nonvolatile liquids work their way downward into the beer still bottoms and are removed as a dilute aqueous stream. The bottoms temperature is approximately 105°C. The bottoms are sent to the DDGS dryer for stillage recycle and DDGS production. The beer still overheads leave the column as 60 percent by weight of ethanol. The overheads product, condensed against cooling water in Figure 3.7 HE-705 and collected in reflux drum Figure 3.7 TW-702, is split into reflux and product, which is sent to the rectifier still Figure 3.7 C-702.

The beer still reboiler duty is provided by three sources: Figure 3.7 HE-707 heats the bottoms against the condensing anhydrous ethanol from the dehydration unit; Figure 3.7 HE-706 provides the remaining steady-state reboiler duty by condensing the rectifier column overheads. A trim steam reboiler, Figure 3.7 HE-704, is provided for fluctuations and startup.

The rectifier column is fed from the overheads of the beer still. The column operates at an elevated pressure of 400 kPa. This elevated pressure raises the column temperature sufficiently to allow heat integration with the dehydration unit. The rectifier column contains 50 trays, which are conventional valve trays. The overhead product, coming off as 190-proof ethanol, is split into two streams: 75 percent is condensed against beer still bottoms in the beer still reboiler, and returned as rectifier column reflux; the remaining vapor is superheated in Figure 3.8 HE-710 by 15°C to prevent condensation in the molecular sieve beds.

The bottoms from the rectifier column, containing 500 ppm ethanol, are used to preheat the beer still feed in Figure 3.7 HE-702. The cooled bottoms are then sent to OSBL for wastewater treatment.

The rectifier column has a side stream leaving from trays 10-15, depending on operation. This side stream contains fusel oils that have formed a separate phase on this tray. Fusel oils are predominantly branched monoalcohols: 40-60 percent isoamyl alcohol, 10-30 percent amyl alcohol, 5-15 percent isopropanol, 5-10 percent n-propanol, and the remainder other 3-5 carbon secondary and tertiary alcohols. Fusel oil composition is a function of the initial feed to the prehydrolysis unit, and the quantity formed is a function of prehydrolysis condition severity. The solubility profiles of fusel oils in water and ethanol result in a tight area where they form a separate phase in one of the column trays. Therefore, they need to be removed to avoid buildup in the column and eventual process upset. The side draw removes the fusel oils, which are then cooled in fusel oils cooler Figure 3.8 HE-712. The cooled fusel oils are subsequently washed in the fusel oils decanter/washer, Figure 3.8 TW-703. The fusel oils are washed counter currently with fresh process water to remove entrained ethanol. The heavy water phase is recycled back to the rectifier still, while the fusel oil phase is decanted and collected in storage facilities. The fusel oils can be blended with fuel-grade ethanol. However, due to their strong odor, they are more often burned in the plant boiler as an auxiliary fuel.

The rectifier column overhead vapors leaving the superheater are then sent to the dehydration unit. The description of this unit is based on data supplied by Delta-T Corporation, for its TSX molecular sieve unit. The dehydration unit is made up of two fixed beds of artificial aluminosilicate zeolite clay. These zeolites are highly regular crystalline structures, containing millions of molecular-sized pores. For ethanol, these zeolites are made with pores of about 3×10^{-10} meters (3Å), which trap water molecules but are too small for ethanol and other impurities. The water is adsorbed into these pores, and the ethanol and other impurities pass through the bed and out the bottom. The molecular sieve can usually contain up to 16 percent of its weight in water. The beds in this process are operated to allow the sieve to accept no more than 50 percent of its capacity. This reduces equilibrium effects in the beds.

The two beds operate on an adsorption/regeneration cycle of about 11 minutes total. The two beds operate at opposite cycles, one regenerating, one adsorbing. The adsorbing bed is fed with high-pressure, superheated 190-proof ethanol. The water is selectively adsorbed, and the anhydrous ethanol (with other impurities) leaves the bottom of the bed and is condensed in the beer still reboiler Figure 3.7 HE-707. The bed under regeneration is placed under vacuum pump K-701. The ejector/liquid ring vacuum pump reduces the pressure in the bed to a slight vacuum (about 90 kPa). The water desorbs from the bed and is condensed in Figure 3.8 HE-711. The water is recycled back to the rectifier column since some ethanol is absorbed in the macropore structure of the zeolite bed. This recycle water is approximately 65 percent water, 35 percent ethanol.

The cooled anhydrous ethanol is sent to a small pasteurization column Figure 3.10 C-704, where any light impurities such as methanol and acetaldehyde are removed prior to product storage. The pasteurization column comprises 20 valve trays, and operates at atmospheric pressure. The overhead product, comprises impurities, is sent directly to the plant boiler as auxiliary fuel. The bottoms are anhydrous ethanol specified to below 500 ppm impurities. This ethanol is sent to product storage.

Any ethanol vented from the fermenters and other process equipment is directed to a vent scrubber. The vent scrubber is a simple packed tower with 20 theoretical trays of random 1-inch Raschig rings for packing. The vent vapors are counter-currently contacted in the column with fresh, cold water. The water absorbs 95 percent of the ethanol entering the vent vapors. The scrubbed gases are sent to the boiler for incineration. The recovered water is sent to the beer still where the captured ethanol is recycled. The returned water stream is preheated by beer still bottoms prior to entering the beer still.

DDGS Separation and Drying

After exchanging heat with the incoming streams to the beer still, the beer still bottoms are collected in an eight-hour surge tank, Figure 3.9 T-801. The surge tank supplies constant flow to the stillage centrifuge Figure 3.9 DC-801, in case of operational interruptions or upstream upsets. The stillage centrifuge separates the solids from the broth, leaving a thick stillage of about 60 percent moisture, and a thin stillage containing the remaining water and minimal solids.

Because most corn dry mill ethanol plants are far from the DDGS by-product market, which is cattle feeding and animal feed preparation, the distillers' grains residue must be dried for storage and transport, otherwise the material would quickly spoil and become unusable. Another, generally more economically attractive option is to integrate the ethanol production with adjacent or nearby livestock feeding operations, so that wet material can be produced and the capital and operating cost (primarily heat energy for drying) can be saved. Such integrated operations are discussed elsewhere in this report.

For drying, the thick stillage is sent to a steam tube rotary dryer Figure 3.9 DC-802 where the material is dried to 10 percent moisture. The dryer is heated with steam supplied from the boiler. The dryer contains a variety of anti-explosion and dust collection devices and auxiliary equipment not shown on the diagram. The dried material is then conveyed to DDGS storage.

The thin stillage is collected in a surge tank, Figure 3.9 T-802. The thin stillage is continuously fed to a three-effect evaporator system. The overhead vapors from the beer still are the primary heat source for the evaporators. During startup, the evaporators are heated by boiler steam; during normal operation, steam supplies trim heat to the evaporators. A portion of the thin stillage is concentrated to about 35 percent syrup and 65 percent water. The syrup is sent to the dryer to be dried and combined with the DDGS. The unevaporated stillage is recycled back into the process, upstream of the fermentation area.

This particular evaporator system comprises three falling film evaporators arranged in a three-effect layout. Falling film evaporators have a practical syrup concentration of 30-35 percent solids. Some plants have used forced circulation flash evaporators, which can increase solids concentration in the syrup up to 45 percent. The use of mechanical vapor recompression (MVR) has been successfully used in cases where steam is not readily available for the evaporators. Because of the use of waste energy in the process as the main evaporator heat source, MVR is not used here.

3.2.2.2 Technology Advances for Corn Dry Milling

A number of companies that engineer ethanol plants have made and continue to make assorted technology advances including in the areas of integrating saccharification and fermentation, improving distillation and dehydration, heat and power cogeneration, overall heat integration, plant water balance, DDGS handling and drying, and additional by-product generation. Among the leaders in this progress are Delta-T, POET (formerly Broin), Fagen, and Katzen.

POET has two new technologies in corn dry mill ethanol production that may significantly improve its economics, embodied in three recently published US patents – 20,050,239,181, 20,050,233,030 and 20,040,234,649 - for cold fractionation and cold cooking. These two process improvements are aimed at reducing the energy needed to convert corn to ethanol and to produce more valuable by-products. Additionally, the cold cooking technology reduces stack emissions. Cold cooking involves grinding and using enzymes to saccharify the starch in the grain without using high temperatures. In the Broin process, no gelatinization conditions are used. Patent 20,050,233,030 also claims continuous fermentation. It appears that this patent may also enable producing oil-yielding germ from dry milling.

3.2.2.3 Corn Wet Milling

As discussed previously, corn can be processed into ethanol using two main routes: wet milling and dry milling. Each process has its own advantages and disadvantages.

Wet milling of corn is the conversion technology utilized when high-fructose corn syrup (HFCS) is desired as the main by-product of ethanol formation. HFCS is often used in combination with or as a substitute for sugar and other sweeteners in many food products, specifically soft drinks and baked goods. The system is highly integrated to disassemble the corn into as many valuable products as possible.

The corn is not actually milled, rather, it is first steeped in a solution of water and sulfur dioxide for 24-48 hours. This loosens the germ and hull fibers. The germ is then removed from the kernel, and corn oil is extracted from the removed germ. The crude corn oil can be further processed as an edible oil plant.

The remaining germ meal from the corn oil extraction is combined with the hulls and fiber to produce corn gluten feed. The corn gluten feed is combined with the heavy stillage from the beer still and dried forming the corn gluten feed. The high protein fraction of the corn kernel is later separated out to produce corn gluten meal, a high-value animal feed made up of about 60 percent protein.

The remaining starch fraction is liquefied and fermented in a process similar to dry milling. In wet milling, often the clear, liquefied starch is split into two fractions: one fraction diverted to ethanol production, and the other fraction used for the production of HFCS or other sweeteners. The amount of liquefied starch diverted to the production of HFCS versus ethanol depends on the relative price and production economics of each product. Therefore, wet mill plants are usually built to produce both swing products to take maximum advantage of economic conditions. Typically, HFCS enjoys a higher margin, and more starch is diverted to HFCS production than to ethanol.

HFCS is a product of the isomerization of dextrose hydrolyzate. Dextrose (D-glucose) is the saccharification product of hydrolyzed cornstarch. Glucoamylase converts the hydrolyzed starch. Since in most cases the purified dextrose is more expensive than HFCS (due largely to crystallizer capital and operating costs), the dextrose solution is more economically converted into HFCS. Essentially, glycose isomerase partially isomerizes the dextrose solution into fructose, producing a mixture of dextrose and fructose. This mixture is further refined and concentrated for sale as HFCS.

The primary capital cost associated with the wet milling plant is the front end, where the corn oil, gluten feed, and gluten meal are separated out. This section normally increases capital costs to more than 75 percent higher than a simple whole-kernel dry milling plant. This capital cost does not include the HFCS processing facilities, which are usually integrated into the ethanol plant.

Process improvements have mainly focused on the steeping area. The state of the art is the continuous sparging of gaseous SO_2 into the steeper tanks. This improves separation between corn components while reducing overall steeping times.

Wet milling is a conversion process used at present in the United States. Archer Daniels Midland, the primary producer of ethanol in the United States, and CPC, a major corn syrup producer, both extensively use this process. It is probable that any future ethanol plants built by these leading companies will be built using the wet milling process, since they would continue to build on their extensive experience in both the ethanol and syrup/sweetener markets. However, since these plants are highly integrated, new entrants would need significant experience before operational proficiency would be developed.

Since these plants would be built predominantly by those companies also interested in sweetener production, with ethanol a more valuable swing byproduct than the main product, this process is not covered in further detail in this report.

3.2.3 Sugarcane to Ethanol

3.2.3.1 Overview

Sugarcane is a tropical crop that has been grown primarily for production of table sugar, molasses, and rum, but is now also the second leading crop after corn for fuel ethanol production. The high sugar content in sugarcane makes it an excellent raw material for ethanol production, and there is a commercial and technical synergy between sugar and ethanol production. Crystal sugar production is optimized when some ethanol is produced, and visa-versa. The sucrose-containing dregs from producing high-value crystal sugar are fed to ethanol production, along with fresh sugarcane juice, stored molasses, juice concentrate, etc. The woody residue from cane juice extraction, called bagasse, is commonly burned in boilers at the mill site to co-produce steam and power for the process, and sometimes extra power for sale to the grid as well. The leading sugarcane producing economies are Brazil, India, China, Thailand, and Pakistan. In Brazil and other regions, liquid processing residue (“vinasse”) is commonly returned to the field, together with bagasse boiler ash as fertilizer. This is one of the several aspects making sugarcane ethanol production a markedly different model from corn ethanol production. Most recently, returning vinasse to the field has been criticized for contaminating groundwater with the salts from the vinasse.

Another important distinction is that cut sugarcane has a shelf life of only a few hours, and at least in Brazil, fresh sugar juice is the primary feed to fermentation, along with other sugar-containing residue streams from sugar production. In Brazil, and in most other tropical sugar-growing areas, there is a dry season during which sugar cane is harvested and a rainy season when harvesting must stop for a number of reasons. The sugar ethanol mill only operates during the dry harvesting season, which is typically only about 200 days per year. This is distinct from corn ethanol, where corn can be stored for use indefinitely, and plants operate as many hours as maintenance needs and economics allow. In India and elsewhere, molasses rather than sugar juice is used, which allows more flexibility in the hours of operation per year.

3.2.3.2 Process Description

Sugar crops include sugarcane, sugar and fodder beets, and fruit crops. Most of the world's sugar is manufactured from sugarcane or sugar beets, with around 70 percent from sugarcane and the balance from sugar beets. The following discussion pertains to fermentation of sugarcane for ethanol production.

Although sugarcane is grown primarily for sucrose and molasses production, it is also used as a raw material for ethanol production. It has a desirable composition for high ethanol yield. The fermentable carbohydrates from sugarcane may be directly utilized in the form of cane juice or in conjunction with a sugar factory from black strap molasses.

Cane juice is prepared by crushing the raw cane and after extraction, clarifying with milk of lime and sulfuric acid to precipitate the inorganic fraction. The resulting extract is a green, sticky fluid, slightly more viscous than water, with an average sucrose content of 12 to 13 percent. It may then be evaporated to the desired concentration and used directly in the fermentation. A major disadvantage in the utilization of sugarcane juice is its lack of stability over an extended period of storage.

Blackstrap molasses is the non-crystallizable residue remaining after the sucrose has been crystallized from cane juice. This heavy viscous material is composed of sucrose, glucose, and fructose at a total carbohydrate concentration of 50-60 percent. Molasses may be easily stored for a long period of time and diluted to the required concentration prior to use.

Sugar Production

As further background for understanding the typically simultaneous or campaign production of cane sugar in the same facility as makes ethanol, the following is a summary of the steps involved in making crystallized white sugar from sugarcane:

- **Juice extraction** - sugarcane is pressed with rollers to extract its juice, or alternatively, is crushed and next passed through a series of soaking chambers through which extraction water is passed counter-currently
- **Purification** - the juice is treated with slaked lime to remove impurities like mud, fiber residuals, etc.
- **Evaporation** - the juice is boiled to evaporate part of the water content and sugar begins to crystallize
- **Raw sugar separation** - the sugar crystals are separated in a centrifuge to remove the syrup, producing raw sugar
- **Refining** - the raw sugar is washed and filtered to remove remaining non-sugar ingredients and color; steps generally include "affination" (wherein raw sugar crystals are treated with a heavy syrup to remove the film of adhering molasses), melting, clarification, de-colorization, evaporation, crystallization, and finishing
- **Storage** - crystals are subjected to final drying with hot air for storage and shipment

It can be seen that it is a complex and expensive process that is typically co-operated with sugarcane ethanol production, and its costs must be appropriately considered with respect to the overall economics of a sugarcane ethanol plant. On the other hand, being able to make sugar from the best fraction and ethanol from the rest (the dregs), is a feature of high efficiency.

Ethanol Production from Sugarcane

A typical process for the ethanol production from cane juice or molasses extracted from sugarcane, consisting of mainly fermentation and ethanol refining, is shown in Figure 3.11. The process is typically run on batch operations, but semi-continuous and continuous operations are also employed.

Typical yields of ethanol from sugarcane including ethanol from bagasse (see Biomass Fermentation later in this section), which were compiled from and cross-checked with various sources, are shown in Figure 3.12. Although Brazilian sugarcane is typically about one-quarter the price of US corn (as is developed below in the economics discussion in this section of the report), it has less far less fermentable carbohydrate content (42.8 percent sugar versus about 72 percent starch). In addition, the figure indicates a yield of ethanol of about 45.1 percent on sugar. This is a little less than the stoichiometric theoretical yield of ethanol from starch/sugar of 0.511 (or 51.1 percent) cited below in this section. In addition, various factors reduce the yield from the theoretical, including use of substrate for yeast metabolism and organics by-products. The US ethanol from corn economics modeled below, in contrast assumes a yield, based on most recent experience, of about 50.3 percent, which is much closer to the theoretical yield.

Figure 3.11 Block Flow Diagram of Ethanol Production from Sugarcane

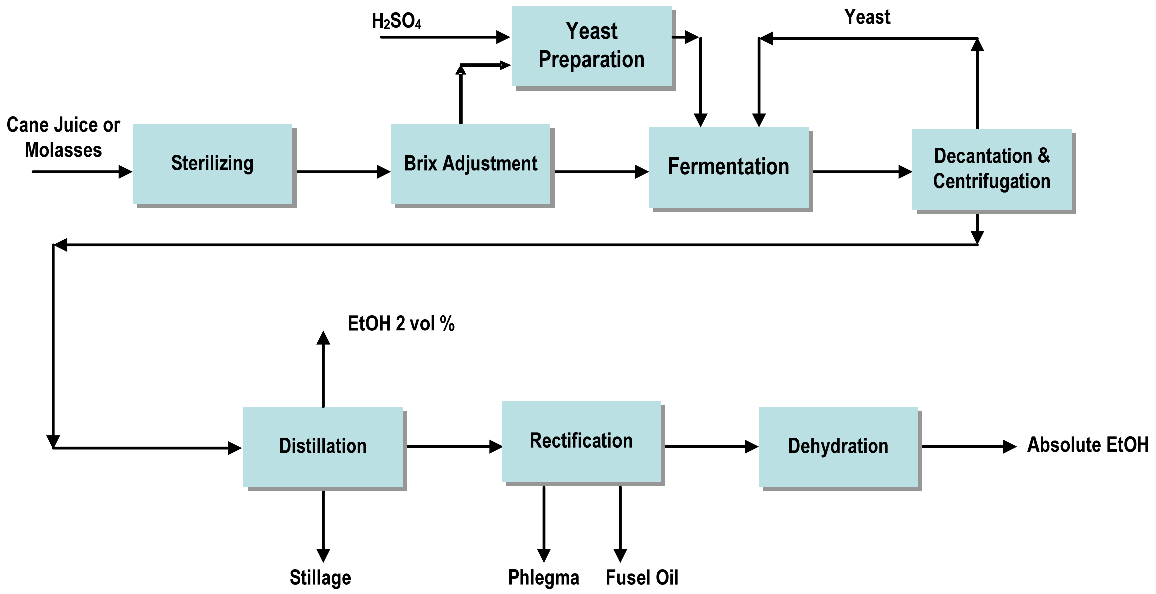
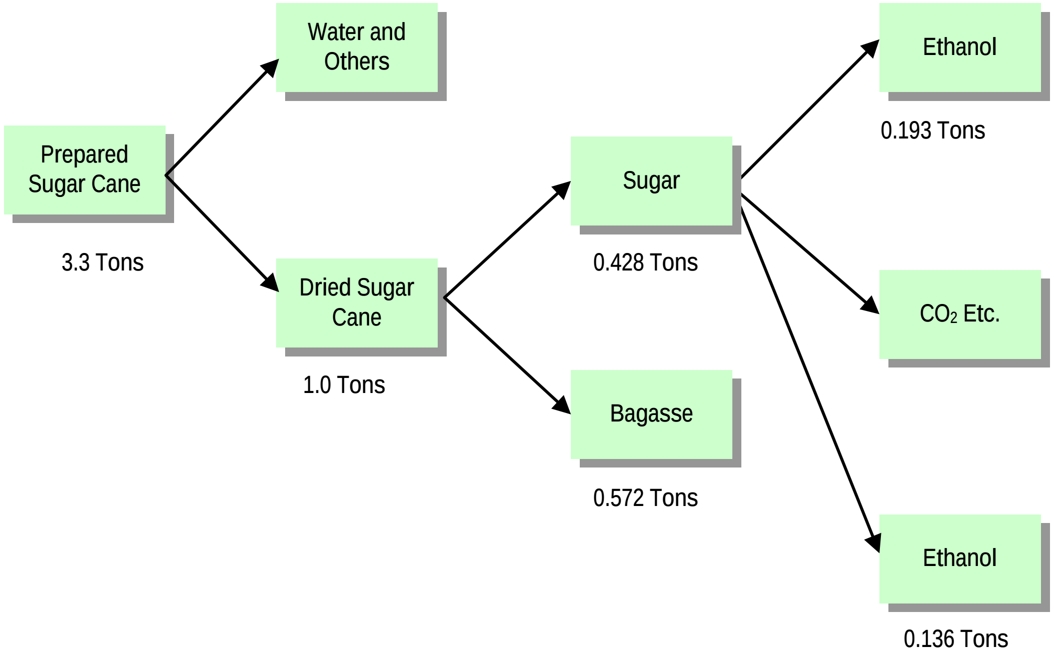


Figure 3.12 Material Balance of Ethanol Production from Sugarcane and Bagasse



The option of using bagasse for additional ethanol production from normal sugarcane, or with specially grown, high-cellulose "energy cane", is being developed by Dedini in Brazil with their DHR process. This process, using mildly acidic ethanol as a lignin solvent and performing a rapid hydrolysis with the extracted cellulose and hemicellulose, is discussed in greater detail below in this section.

3.2.4 Other Starch/Sugar Feeds to Ethanol

3.2.4.1 Sugar Beet

Sugar beet, similar to sugarcane, containing carbohydrates that consist primarily of sucrose, can also be used as raw material for ethanol production. Sugar beets are primarily grown in cooler regions of the temperate zone. Further details of sugar beet producers are given in Section 4, Feedstocks.

3.2.4.2 Cassava

Cassava is a root crop throughout the tropics and in parts of South America. Cassava roots are very rich in starch and have been considered by the cassava producing economies for ethanol production. Further discussion of cassava can be found in Section 4, Feedstocks.

3.2.5 Lignocellulosic Biomass to Ethanol

3.2.5.1 Overview

Biomass fermentation will need to compete with thermochemical routes for producing liquid biofuels. There are fundamental challenges in converting cellulosic biomass to liquid biofuels, whether by enzymatic or thermochemical routes, and even more for fermentation routes. Some of these are:

- Availability of inexpensive feedstock
- Storage of feedstock (which is often seasonally produced), without degradation for continuous feeding to the process over the year
- Transport of feedstock to the processing facility
- Physical treatment of feedstock (cleaning, milling, chopping, and grinding)
- Obtaining a sufficient volume of biomass feedstock at one site economically
- Reliable and efficient conversion of feedstock to fuel

In addition, thermochemical routes are especially challenged by the typical high water content of most lignocellulosic biomass resources, which is generally not a problem for fermentation processes. Fermentation processes can be at risk of “poisoning” by phytotoxins (such as aflatoxins, penicillins, and others) typically produced by molds and fungi growing on moist biomass.

Biomass is comprised of complex structures that are difficult to separate into basic components for fermentation processing. It is made up of a number of different components, generally including:

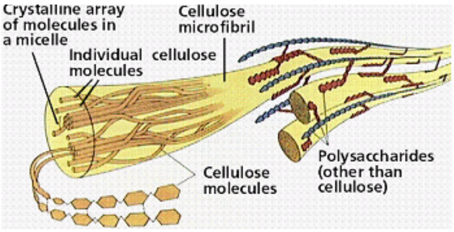
- 40-60 percent Cellulose - Cellulose is a polymer of glucose molecules (6-carbon sugars) that have a beta 1-4 linkage. This bond is resistant to chemical attack due to the high degree of hydrogen bonding that can take place between the aligned strands. These bonds block the entry of chemicals or enzymes that could cleave the linkage between glucose molecules

- 20-40 percent Hemicellulose - Hemicellulose is a polymer made of 5-carbon sugars (usually xylose and arabinose), 6-carbon sugars (galactose, glucose, and mannose) and uric acid. Hemicellulose is highly branched and, unlike cellulose, is easy to convert (via hydrolysis) into its constituent sugars. The difficulty that hemicellulose poses for ethanol production is that xylose and arabinose, as well as galactose and mannose are difficult to convert to ethanol by using most known microbes
- 10-25 percent Lignin - Lignin is a large hydrophobic (mostly aromatic) polymer composed primarily of amino acids, one of the most important being phenylalanine. The exact structure of lignin varies not only among plant species, but within species if members of populations are exposed to different environmental conditions (both biotic and abiotic)

Both cellulose and hemicellulose are hydrophilic and are at risk of being degraded when exposed to moisture. Therefore, lignin provides the important function of allowing the structural components of plants to be watertight.

Finally, the physical arrangement of biomass within the plant cell makes rapid conversion harder. The structure of cellulosic biomass is conceptually represented in Figure 3.13.

Figure 3.13 Conceptual Structure of Cellulose in Plants



Pretreatment

Because lignocellulosic biomass is by nature designed to be recalcitrant to the enzymatic attacks mounted by life forms in the environment that would feed on it, pretreatment technologies need to be used to overcome this recalcitrance to reduce the difficulties and costs of subsequent steps. Pretreatment technologies can utilize dilute acid, lime treatment, steam explosion, ammonia fiber explosion (AMFE or AFEX), organic solvents, or other processes to disrupt the hemicellulose/ lignin sheath that surrounds the cellulose in plant material. These and other important technologies commercially available or under development are shown in Table 3.4. Each of these technologies has advantages and disadvantages in costs, yields, material degradation with respect to subsequent processing objectives, other downstream processing impacts and needs, and generation of process wastes.

One of the most advanced and promising pretreatment technologies, which the US DOE has considered for some of economic projected analyses, Ammonia Fiber Explosion (AFEX), employs liquid ammonia under moderate heat and pressure to separate biomass components.

However, the technology for which perhaps there is the most experience is dilute acid hydrolysis. Others are focused on organic solvent processes with pH adjustments.

NREL – Novozymes and Genencor

While the details of the new biomass to ethanol processes are considered to be proprietary, there have been a number of publications that generally describe the dilute acid route to biomass ethanol. A major contributor in this area has been the National Renewable Energy Laboratory (NREL) which has been working in this area for two decades and has built significant expertise. NREL (Office of the Biomass Program) has most recently and significantly co-funded and collaborated in a $40 million with the private biotech companies Novozymes and Genencor to advance the biotechnology related to the efficacy and cost of enzymatically converting biomass to sugars and next to ethanol in a program that was announced as completed in 2006. This program focused on enzyme biochemistry, cost, and specific activity, and investigated interactions between pretreatment and enzymatic hydrolysis. The claimed result was estimated 30-fold reductions in the cost burdens of enzyme in the processing of biomass, in terms of $ per gallon of ethanol. Enzyme-related costs that had been over $3.00 per gallon now are claimed to be closer to just over $0.10 per gallon.

Among other related programs the US DOE has operated the biomass refining Consortium for Applied Fundamentals and Innovation (CAFI) program for supporting academic research groups advancing a set of lignocellulosic pretreatment options (dilute acid, lime, AFEX, hot water, etc.). Other organizations are reported to be researching lignocellulosic-based ethanol production via fermentation routes or planning projects based on various types of biomass, including Iogen (Canada/United States), Dedini (DHR Process, Brazil), Abengoa Bioenergy (Spain), and BCI (United States).

Iogen

Iogen is operating a facility in Ottawa, Canada, utilizing proprietary enzyme hydrolysis and fermentation techniques and feeding mainly wheat straw to produce 260 thousand gallons per year of ethanol. Shell and Morgan Stanley are reported to be investors in the company. Iogen has announced plans for a 40 million gallon per year facility in western Canada, the United States, or Germany with a $350 million expected cost. This level of investment is 5-7 times higher than for conventional ethanol production from grain in the United States. Beyond this, Iogen has been closed with information about their process that would be useful for evaluative purposes.

Table 3.4 Comparison of Lignocellulosic Pretreatment Technologies

	Residence Time	Temperature	Pressure	Other Conditions
Chemical				
Acid-Catalyzed				
Autohydrolysis	~ 1 hour	~200 °C	~15 °atm	
Steam Explosion	0.3-50 minutes	190-250 °C	12-40 atm	
Liquid Hot Water	2-15 minutes	190-220 °C	13-25 atm	
Liquid Hot Water (Natural pH)	-15 minutes	160-220 °C	6-25 atm	
Dilute Acid				
(H_2SO_4, SO_2, HCl, HNO_3)	5-30 minutes	140-190 °C	4-13 atm	0.5-10 percent acid
Concentrated Acid (H_3PO_4)	30-60 minutes	0 °C	1 atm	85 percent H_3PO_4
Paracetic Acid ($C_2H_4O_3$)	1-180 hours	25-75 °C	1 atm	2-10 percent $C_2H_4O_8$
				0.2-1.0 g $C_2H_4O_3$/g biomass
Supercritical Carbon Dioxide	1 hour	35-80 °C	70-270 atm	
Base-Catalyzed				
Sodium Hydroxide	24-96 hours	25 °C	1 atm	1 percent NaOH, 01. g NaOH/g biomass
Lime ($CA(OH)_2$)				
Low Ligin Content				
(12-18 percent)	1-2 hours	100-120 °C	1-2 atm	0.10 g $Ca(CH)_2$/g biomass
Medium Ligin Content				
(18-24 percent)	~30 days	~55 °C	1 atm	0.10-0.15 g $Ca(OHO)_2$/g biomass
High Ligin Content				
(>24 percent)				0.15-0.20 g $Ca(OHO)_2$/g biomass
Wet Oxidation	15 minutes	185 °C	15 atm	0.6 percent Na_2CO_3
Ammonia (NH_3)				
ARP	~ 15 minutes	~ 180 °C	~ 20 atm	15 percent NH_3
AFEX	~ 5 minutes	60-100 °C	~ 20 atm	1 g NH_3/g biomass
Oxidative Alkali				
(NaOH + H_2O or O_3)	6-26 hours	20-60 °C	1 atm	1-15 percent H_2O_2 or O_3. pH = 11.5
Solvents				
Organosly	60 minutes	20-60 °C	1 atm	1.25 percent H_2SO_4, solvent = 60 percent ethanol
Cellulose Solvents	Generally not viable for industrial applications			
Physical				
Comminution	Does not significantly improve digestibility			
Ball Milling	Not economically viable			
Compression Milling	Not economically viable			
Radiation	Not economically viable			
Biological				
Fungi	Not yet commercially feasible			

Source: "Producing Fuels and Chemicals from Lignocellulosic Biomass", Sierra et. Al, p. S11, CEP, August 2008 Special Edition

Dedini DHR Process

Dedini is involved in about 80 percent of the sugarcane-based ethanol capacity in Brazil. DHR ("Dedini hidrólise rápida"), or rapid hydrolysis, is a version of the ethanol Organosolv wood pulping process (long under development in Europe, North America, and elsewhere), with a very dilute acid hydrolysis, integrated with fermentation and distillation, for ethanol production from sugarcane bagasse. Dedini has discussed the process on a limited basis at public conferences.

Dedini says they first developed DHR in the 1980s, with the approval of and financing by Brazilian government agencies and with support from the World Bank, and that patents have been issued in the United States, EU, Canada, Mexico, Brazil and Russia, with applications made in Japan and other economies.

Dedini claims to have analyzed 26 lignin solvents before choosing ethanol (even though ethanol is the standard solvent for Organosolv). They claim that DHR addresses many problems of lignocellulosic fermentation by using a strong lignin solvent, at high temperatures, which enables rapid access to cellulose and hemicellulose, after the lignin has been dissolved. This allows very fast sugar formation (in minutes), which raises yields. The hydrolysis medium, because of the efficacy of the lignin solvent, can use a minimum acid concentration. Immediate removal of the sugar formed, with rapid cooling of the hydrolyzed product, interrupts sugar heat degradation. The sugar obtained is stabilized by rapid neutralization of the hydrolyzed product.

Dedini claims to have developed and operated a pilot plant of 100 liters per day ethanol production, currently installed at a CTC-Copersucar facility, with a technical cooperation agreement between Dedini and Copersucar, signed in 1997. A five thousand liter per day semi-industrial plant was installed in late 2002 at Dedini Group's São Luiz sugar and alcohol plant, in Pirassununga, SP, Brazil. This was a cooperative project of Dedini, Copersucar and FAPESP (São Paulo State Research Agency). This facility is in a continuous operation stage, developing engineering parameters for a full-scale industrial plant design. Figure 3.14 displays the Dedini pilot plant which is producing ethanol from bagasse.

Figure 3.14 Dedini Pilot-Plant for Producing Bagasse-Based Ethanol

Source: Dedini S/A Industrias de Base

Abengoa Bioenergy- BCyL

Abengoa is the largest ethanol producer in Europe (current capacity of 340 million liters/year) and one of the largest in the world. Its US subsidiary, Abengoa Bioenergy (formerly High Plains Corporation), which is number five in the US market, owns and operates ethanol plants in Kansas, Nebraska and New Mexico with a total production capacity of 100 million gallons per year. Abengoa Bioenergy is developing a semi-commercial scale biomass plant to demonstrate their BCyL biomass-to-ethanol process technology. Construction began in August, 2005 on the plant located in Babilafuente, Salamanca, Spain. They commissioned the start at the end of 2007. Abengoa aims to process 70 tons per day (23 thousand tons per year) of agricultural residues, such as wheat straw, to produce over 5 million liters (4 thousand tons per year, or 1.25 million gallons per year) of fuel grade ethanol per year. Few other details have been provided by Abengoa.

However, Toronto, Canada-based SunOpta Inc. announced signing a US$ 6.1 million contract in 2005 to supply its patented steam explosion equipment and process technology to the project. SunOpta states that if the wheat-straw-to-ethanol project in Spain is successful, the company will move forward with "clipping on" cellulosic ethanol plants at its US facilities.

Abengoa Bioenergy R&D (ABRD) is providing its proprietary process technology and the process engineering design for the BCyL Biomass Plant. The project goals are to commercially demonstrate the process and to optimize plant operations. Besides ethanol, the plant is expected to generate fermentation residues for the development and testing of co-products, such as animal feeds and chemicals. ABRD implemented the second phase of this project in the fall of 2007 in which processed biomass undergoes fractionation, a technology currently under development, to extract lignin, pentose sugars, and manufacture feed products.

Abener, Abengoa's EPC arm, is developing the detailed engineering design. Abener is also responsible for the plant construction, which was completed in 2006. Figure 3.15 is an aerial view of the Biomass Plant, being developed next to the 195 million liter per year grain ethanol plant. Abengoa claims that co-location and integration of biomass ethanol production with a grain ethanol plant leads to reduced capital and operating costs for the biomass plant.

Figure 3.15 Site View of Abengoa's BCyL Biomass Plant

Source: Abengoa

BCI - BC International Corporation

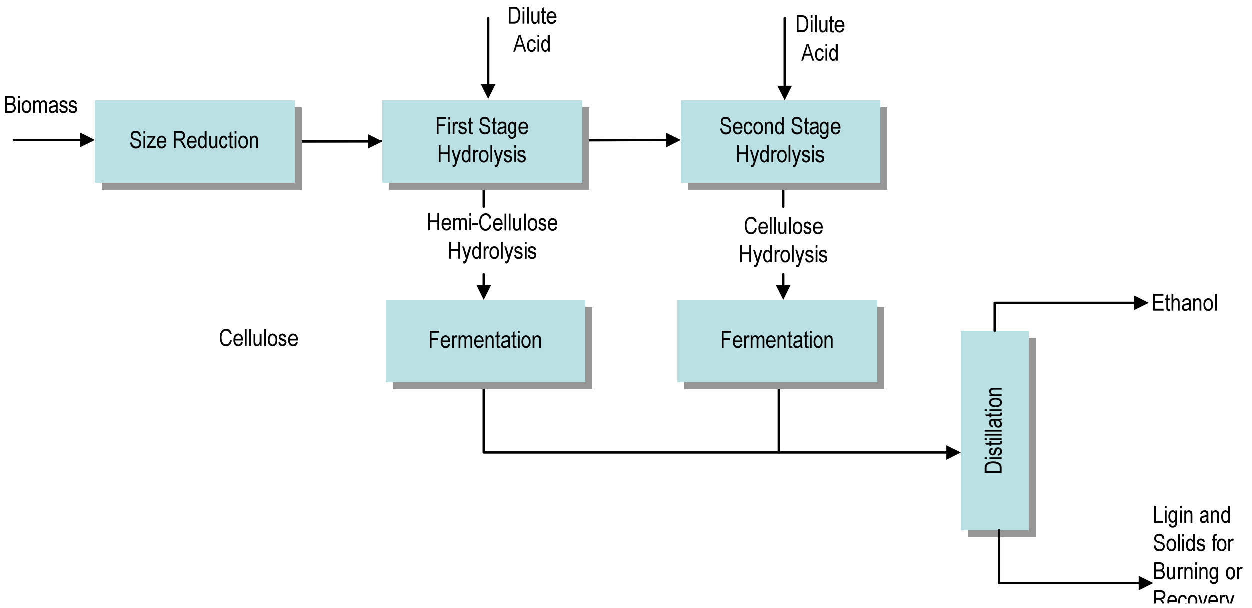
BC International Corporation (BCI), a privately held company headquartered in Dedham, MA was founded in 1992, originally as BIONOL Corp., to develop a paper mill sludge-to-ethanol project in New York State. Also participating was BioEnergy International, which held rights to University of Florida (UFL) technology for conversion of C_5 as well as C_6 sugars to ethanol at claimed high yields. BCI, BioEnergy, and UFL operated tests on a 100 pound per hour hydrolyzer producing 10 pounds per hour of fermentable sugars from corn stover, bagasse, and hardwood chips. The recovered sugars were fermented in a variety of pilot scale units. BCI claims to be the exclusive license holder of the technology that emerged.

BCI is allied with two companies, ICF Kaiser and TIC, for the design and construction of the first commercial plant, and is also receiving support from the United States. DOE for process validation and a commercial demonstration plant being built at Jennings, LA.

The unique aspect of this company's technology is the genetically modified organism based on an E. coli bacterium with the ethanol production genes of zymomonas spliced into it. This was developed by Dr. Lonnie Ingram of UFL, for which he was recognized in a Congressional ceremony with the issuance of a special patent number 5,000,000. The recombinant organism is claimed to ferment both hexose and pentose sugars with over 90 percent efficiency, and to have high ethanol tolerance, stability, pH and temperature tolerance and a wide substrate range, including sugar oligomers. The process is claimed to therefore be ideally suited to handle biomass feedstocks that produce both C_5 and C_6 sugars upon hydrolysis.

The rest of the BCI process is based on established technology for the basic steps of feedstock handling, hydrolysis, and product recovery. It uses a two stage dilute acid hydrolysis to prepare the sugar stream, first releasing the hemicellulose and next the cellulose. Both stages are at elevated temperatures and pressures and use dilute sulfuric acid to reduce reaction time. There are two separate fermentations, although both use the same organism. The process is illustrated in Figure 3.16.

Figure 3.16 BC International Process



Soure: "World Ethanol Report", Environment Canada, 1999.

The two-stage dilute acid process dates to the 1940s, continuing in the 1950s with Tennessee Valley Authority (TVA)/USDA pilot plant studies. TVA's work on the process ceased in the late 1980s. Problems persisted in fermenting the pentose sugars and high capital costs relative to grain based plants.

TVA data will be used in the design, modification, and conversion of an inactive grain-based ethanol plant in Jennings, LA which is now owned by BCI.

Nexant served as a market consultant to this project for ethanol that would be marketed as industrial grade (similar to fuel ethanol).

There have been some concerns expressed about using the E. coli bacterium in an industrial application, but the USDA has determined that the recombinant organism does not require a permit for interstate commerce. The E. coli cell mass generated in the fermentation would be used as a boiler fuel to provide energy to the plant. Like other processes for lignocellulosics, energy consumption is higher than in a grain-fed process, because of a more difficult feedstock and more dilute solutions handled, among other reasons. However, as with other lignocellulosic processes examined herein, depending on the biomass feedstock, much if not all of this energy can be supplied by gasifying and/or combusting lignin, unconverted sugars, and other waste biomass at lower cost and with less global warming impact than if fossil fuels were used.

BCI has signed a letter of intent with the City of Gridley, CA to develop a 20 million gallon per year facility using rice straw and other biomass as feedstock for ethanol production.

BCI has not published much information on estimated operating or capital costs, but the limited public information available indicates that the project, even though it would reuse the Jennings facility, would have a capex on the order of about $7 per annual gallon of ethanol production, which is 5-7 times higher than grain-based production, and about the same as is being publicly discussed for Iogen's proposed project. Of course biomass feeds could be far cheaper than grain or sugar feeds or essentially free, or yielding a tipping fee.

Switchgrass-Based Lignocellulosic Ethanol

Switchgrass has been prioritized by US DOE program funding as a bio-energy crop of choice and was featured in the comments on the energy crisis in last US Presidential State of the Union Address.

Switchgrass' prospects as an energy crop highlight the potential role of genetic engineering in improving agronomic traits such as yield, mowing ease, and phased maturation (since storage against single-season harvesting is a major challenge of bio-based industry development). In Brazil, as well as eventually in the United States, there is similar interest in "energy cane", a type of cane developed by conventional breeding and/or by genetic modification. This cane grows faster, with less agronomic inputs, and with greater biomass yield at the expense of a lower sugar yield. The leading biotech company, Ceres Inc., and other entities are working on this crop as well as on switchgrass improvement. Much of the following discussion of switchgrass issues can also apply to energy cane.

Iowa and other Heartland states are testing and promoting switchgrass cultivation, and would welcome and assist in funding and in other ways, switchgrass-based project development. Switchgrass is compositionally similar to corn stover for fermentation and combustion applications, and to wood for gasification, but is in many ways better. Its cultivation for combustion and gasification applications can be leveraged for fermentation projects. Switchgrass supply has many advantages, besides federal Administration support, including cost, public perception, and being unlinked from the corn harvest cycle (in contrast to corn stover). Switchgrass fermentation is on a pathway to major improvements in 5-10 years.

In the developing global system of carbon emission reduction credit trading, avoiding such emissions is beginning to have real economic value. However, the United States is not party to the Kyoto Protocols that set targets for emissions reductions to drive this market, individual companies and states are setting targets of their own. Growing switchgrass also lays down a large mass of roots that sequesters carbon for many years and may have additional value under this trading system. For this study, corn stover-based lignocellulosic fermentation is described in detail, but in the section on economics of current and future technologies, switchgrass is the model.

By-product energy credits proved critical to achieving viable economics for biomass fermentation. For this, it was assumed, based on previous work by others and a consensus of expert opinions, that about $0.018 per kWh would be a reasonable trading credit for CO_2

emissions reductions by using biomass rather than coal for utility power generation (related to an imputed “carbon tax” of $50-75 per ton). Another enhancement to sales to the grid of power generated from biomass is the so-called “green power price” which represents a pass through to the generator of a price premium customers can elect to pay for power generated from clean sources, including typically, hydro, wind, photovoltaics, and biomass combustion. This ranges from $0.005 per kWh to $0.03 per kWh.

Other Biomass

According to the US Congress, “the term biomass means any organic material that is available on a renewable or recurring basis, including dedicated energy crops, trees grown for energy production, wood waste and wood residues, plants (including aquatic plants, grasses, and agricultural crops), residues, fibers, animal wastes and other organic waste materials (but not including non-segregated municipal solid waste (garbage)).” (US Congress, H. R. 1294, 2004). Corn kernel hulls, corn stover, bagasse (residues of crushed sugarcane), and rice straw, contain cellulose like switchgrass does. The cost of harvesting and transporting the residue depends on the per acre residue yield.

Corn Stover, Wheat Straw, Soybean Hulls etc.

Corn stover, wheat straw, and soybean hulls are residues of corn, wheat and soybean harvesting, are relatively abundant agricultural residues geographically coincident with corn (Midwest) and wheat (Plains and Northwestern states). Following a harvest, residues such as stover or wheat straw are baled, wrapped in a plastic mesh, and transported to the edge of the field. Once at the fields edge, the stover is transported to an energy facility in such a manner that 10 days of inventory are kept. However, removal of corn stover and wheat straw risks degrading soil quality and long-term productivity. Corn stover and wheat straw supply models need to consider residue levels needed for erosion control and soil carbon maintenance. Switchgrass, energy cane, and such crop residue production will compete with each other and other crops for agricultural land. As bio-energy and biomaterials production increases, demand for land for corn, wheat, soybeans, and switchgrass production will increase relative to other crops. This will shift agricultural markets and land use patterns, and crop production levels and prices. The dynamics of the existing crops are more complex and more vulnerable to disruptive dynamics than switchgrass.

Virgin Wood and Wood Waste

Vast quantities of wood wastes are available from forest thinning and from growing virgin wood resources, but the pattern of these resources are geographically and logistically so fragmented and different from switchgrass, that Nexant decided it would be inappropriate and unnecessary to include them as comparative cases.

Other Agricultural Wastes

Other agricultural wastes could include cattle and swine manure and poultry litter. Again, though the concentrations of these resources can be very high where they are generated, they often contain high levels of water based on how they are generated, are problematic to store and handle, will generally support only relatively small energy operations, and are thus not comparable to the industrial model of switchgrass. These wastes are much more commonly aimed at anaerobic digestion processes.

Municipal Solid Waste

Municipal solid waste, or MSW, has many issues. A major distinguishing factor is the concept of “tipping fees”, or being paid for taking the MSW to use as feed. However, against this are handling and storage issues with the presence of putrefiable components, the need to separate and dispose of non-organic or non-combustible components, which are potentially toxic components.

US DOE Genomics to Liquids (GTL) Program

The Genomics to Liquids (GTL) research program focuses on developing technologies to understand and use the diverse capabilities of plants and microbes to create innovative solutions to the world’s energy challenges. In particular the program has focused on cellulosic ethanol. Some of its research targets include:

- **Improving Cellulase Systems**. GTL will accelerate the development of optimal cellulase systems by providing resources for screening thousands of natural and modified enzyme variants, enabling the high-throughput production and functional analysis of these enzymes, elucidating regulatory controls and essential molecular interactions, and developing models for analyzing the structure and activity of natural and engineered enzyme systems
- **Enabling the Development of Integrated Bioprocessing**. A long-term target for GTL research is integrated bioprocessing, the conversion of biomass to ethanol in a single step. Accomplishing this requires the development of a genetically modified, multifunctional organism or a stable mixed culture capable of carrying out all biologically mediated transformations needed for the complete conversion of biomass to ethanol.

In June 2007, DOE announced the Office of Science has established three Bioenergy Research Centers intended to accelerate basic research in the development of cellulosic ethanol and other biofuels as part of the Office's Genomics: GTL Program.

US DOE Lignocellulosic Bio-refinery Projects

The US DOE is involved in four commercial scale bio-refinery development projects with outside companies, which are described below:

- Abengoa Bioenergy Biomass, LLC (Hugoton, Kansas) – converting lignocellulosic feedstocks (corn stover, wheat straw, sorghum, switchgrass) to produce both ethanol and syngas, with 11.4 million gallons of ethanol per year. Also co-producing steam for cellulosic ethanol operations and excess steam for corn ethanol plant nearby. Estimated construction and start up in 2010 and 2012, respectively
- Range Fuels (formerly Kergy Inc.) (Soperton, Georgia) – converting biomass (comprised of unmerchantable timber and forest residues) to produce 935 thousand gallons of ethanol and 935 thousand gallons of methanol. Using pyrolysis followed by thermal reforming of pyrolysis vapors for biomass conversion. Estimated start up is the first quarter of 2010

- Poet (formerly Broin Companies) (Emmetsburg, Wisconsin) – converting lignocellulosic feedstocks (corn cobs and/or corn fiber) to produce 25 million gallons of ethanol per year. Integrating the production of cellulosic ethanol into a dry corn mill process. Production is estimated to start in 2011
- BlueFire Ethanol, Inc. (Mecca, California) – converting biomass (comprised of sorted green waste and woody waste from landfills) to produce 19 million gallons of ethanol per year. Using their concentrated acid hydrolysis technology followed by fermentation for biomass conversion. Facility will be located next to a 47MW biomass fed power plant. Project is currently delayed

The DOE is also involved in nine small-scale bio-refinery development projects. The projects include:

- Ecofin, LLC (Alltech Envirofine, LLC) (Washington County, Kentucky) – converting a wide range of lignocellulosic feedstocks (corn cobs) to produce more than 1 million gallons of cellulosic ethanol by fermentation. Estimated construction and start up in 2010
- Flambeau River Biofuels LLC (Park Falls, Wisconsin) – converting woody biomass (mill residues and unmerchantable forest biomass) to produce 9 million gallons of Fisher-Tropsch (F-T) green diesel and 50 million pounds of F-T wax. Facility will be located next to Flambeau River Papers' pulp and paper mill to replace natural gas use. Utilizing ThermoChem Recovery International, Inc. (TRI) gasification and F-T catalyst conversion. Estimated construction and start up in 2009 and 2011, respectively
- Mascoma (Monroe County, Tennessee) – converting woody biomass (hardwoods) to produce 5 million gallons of ethanol per year. Using hemicellulose and cellulose pretreatment and conversion to fermentable sugars to make ethanol and other products. Estimated construction in 2010 with start up around 2011
- NewPage Corp. (Wisconsin Rapids, Wisconsin) – converting woody biomass (mill residues and unmerchantable forest biomass) to produce 5.5 million gallons of F-T liquids per year, specifically renewable diesel. Using TRI gasification for production. Estimated construction and start up in 2010 and 2011, respectively
- Verenium Biofuels Corporation (Jennings, Louisiana) – converting sugarcane bagasse, dedicated energy crops, agricultural waste and wood product residues to produce 1.5 million gallons of ethanol per year. Lignocellulosic feedstocks go through pretreatment, enzymatic hydrolysis and then the sugars are fermented into ethanol. Completed start up with optimization continuing through 2009
- ICM Incorporated (St. Josephs, Missoui) – converting various feedstocks (corn fiber, switchgrass, corn stover and sorghum) to produce 1.5 million gallons of fuel ethanol per year. The facility will be located next to an existing 50 million gallon per year ethanol plant to leverage energy usage and infrastructure. Estimated start up is the fourth quarter of 2010
- RSE Pulp & Chemical, LLC (Old Town, Maine) – converting the hemicellulose extract from woody biomass to produce 2.2 million gallons of cellulosic ethanol per year. The

facility will be located next to RSE's existing pulp and paper mill. Estimated to start up in 2010

- Pacific Ethanol, Inc. (Boardman, Oregon) – converting wheat straw, corn stover and popular residuals to produce 2.7 million gallons of ethanol per year. Approximately 15 percent of the material will be separated out as a solid fuel that can be used for combustion. Facility is using BioGasol proprietary conversion technologies which consist of pretreatment hydrolysis, fermentation, and anaerobic digestion of process water and recirculation. Project is currently delayed
- Lignol Innovations, Inc. (Commerce City, Colorado) – project is cancelled

3.2.5.2 Design Parameters and Feedstock Characteristics

NREL's process and economic model of the conceptual lignocellulose-to-ethanol process was initially developed in 1995. The model has been refined each year and was published in NREL's Technical Reports in 1999, 2000 and 2002. Table 3.5 outlines the overall design parameters that were used in the model.

Table 3.5 General Design Parameters of NREL Bioethanol Process

Process:	Dilute Acid / Enzymatic Hydrolysis
Feedstock:	Corn Stover
Plant Type:	Stand Alone
Location:	Undetermined
Fuel Ethanol Production:	25 and 56 Million Gallons per Year

The feedstock used in the process is corn stover, the residue from harvesting corn, which is left in the fields after harvesting or used, is as livestock fodder. It has been identified as a likely near-to mid-term agriculture residue feedstock for the lignocellulose-to-ethanol process. Corn stover has a high carbohydrate content and can be collected in a sustainable fashion.

Corn stover contains considerable quantities of cellulose, a beta-linked glucose polymer, which is more difficult to break down to glucose monomers than the alpha-linked polymer in starch. In addition, it contains hemicellulose, which is a more complex polymer of several sugars. The predominant sugars in hemicellulose are xylose and arabinose. These five-carbon sugars can also be fermented to ethanol with the proper microorganism. The maximum theoretical yield from corn stover with the composition listed in Table 3.6 is 107 gallons per dry ton (or 91 gallons per ton at 15 percent moisture). For this analysis, a yield of 69 gallons of pure ethanol per dry ton was used, which equates to an average yield of 65 percent of the cellulose and hemicellulosic polymers.

Table 3.6 Corn and Stover Compositions

Corn	% Dry Basis	Corn Stover	% Dry Basis
Component		Component	
Starch	72	Cellulose	37.3
Hemicellulose/ Cellulose	10.5	Galactan/Mannan	1.4
Protein	9.5	Xylan	20.6
Oil	4.5	Arabinan	2.1
Sugars	2	Lignin	17.5
Ash	1.5	Ash	6.1
		Acetate	2
		Extractives	13
Total	100	Total	100
% Moisture	15	% Moisture	15

Entwined around the two sugar polymers is lignin, a hydrophobic and largely aromatics-based polymer that does not contain sugars. Lignin, like the fiber in corn, has potential by-product value. The fiber by-product, along with yeasts, sugars, and other fermentation residues, is sold as “Distillers’ Dried Grains and Solubles”, or DDGS. Lignin, currently recognized for its fuel value, may have a better co-product value as a chemical feedstock, which has long been discussed and researched, but is as yet unrealized.

Stover is typically 15 percent moisture, although it can vary depending on age, growing conditions, and variety.

Because the collection of stover is a new industry, there is little data on the collection costs. Demand for stover from an established lignocellulosic ethanol industry could escalate the price.

3.2.5.3 Process Description

Overview of Lignocellulosic Biomass to Ethanol

The process used in the analysis can be briefly described as using co-current dilute acid prehydrolysis of the lignocellulosic biomass with simultaneous enzymatic saccharification of the remaining cellulose and co-fermentation of the resulting glucose and xylose to ethanol. In addition to these unit operations, the process involves feedstock handling and storage, product purification, wastewater treatment, enzyme production, lignin combustion, product storage, and other utilities. Soluble carbohydrate residues from the process are anaerobically digested to produce fuel biogas for the process, and other residues, including lignin, are combusted in a fluid bed system (similar to those used for black liquor in the pulp and paper industry).

Table 3.7 summarizes the major process areas of NREL's bioethanol process. The overall process flow diagram of NREL's conceptual design is elucidated in Figure 3.17.

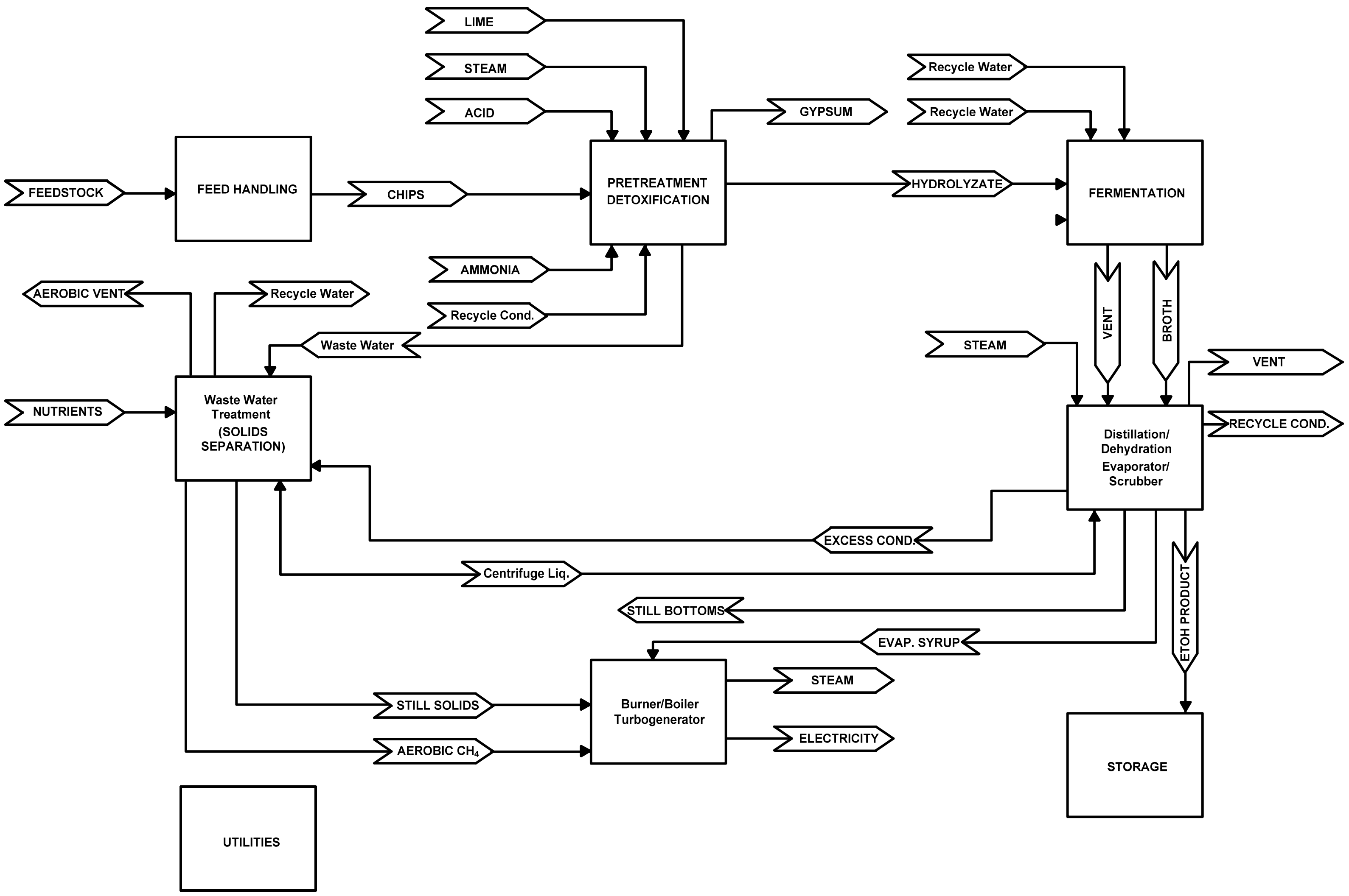
Table 3.7 Major Unit Operations of NREL Bioethanol Process

1.	Feedstock Storage and Handling
2.	Pretreatment and Hydrolyzate Conditioning
3.	Saccharification and Co-Fermentation
4.	Product, Solid, and Water Recovery
5.	Wastewater Treatment
6.	Product and Feed Chemical Storage
7.	Burner Boiler and Turbogenerator
8.	Utilities

Corn stover (comprised of stalks, leaves, cobs, and husks), is delivered to the feed handling area for storage and size reduction. From there the biomass is conveyed to pretreatment and detoxification. In this area, the biomass is treated with dilute sulfuric acid catalyst at a high temperature for a short time, liberating the hemicellulose sugars and other compounds. Separation with washing removes the acid from the solids for neutralization. Over-liming is required to remove compounds liberated in the pretreatment that are toxic to the fermenting organism. Detoxification is applied only to the liquid portion of the hydrolysis stream.

Enzymatic hydrolysis (or saccharification), together with co-fermentation of the detoxified hydrolyzate slurry, is carried out in continuous hydrolysis tanks and anaerobic fermentation tanks in series. A purchased cellulase enzyme preparation is added to the hydrolyzate in the hydrolysis tanks that are maintained at a temperature to optimize the enzyme's activity. The fermenting organism Zymomonas mobilis is first grown in a series of progressively larger batch anaerobic fermentations to make enough cells to inoculate the main fermenters. The inoculum, along with other nutrients, is added to the first ethanol fermenter along with the partially saccharified slurry at a reduced temperature. The cellulose will continue to be hydrolyzed, although at a slower rate, at the lower temperature. After several days of separate and combined saccharification and co-fermentation, most of the cellulose and xylose will have been converted to ethanol. The resulting beer is sent to product recovery.

Figure 3.17 NREL Lignocellulosic Biomass to Ethanol Process



Product recovery involves distilling the beer to separate the ethanol from the water and residual solids. A mixture of nearly azeotropic water and ethanol is purified to pure ethanol using vapor-phase molecular sieves. Solids from the distillation bottoms are separated and sent to the boiler. Concentration of the distillation bottoms liquid is performed by evaporation using waste heat. The evaporated condensate is returned to the process and the concentrated syrup is sent to the combustor.

Part of the evaporator condensate, along with other wastewater, is treated by anaerobic and aerobic digestion. The biogas (high in methane) from anaerobic digestion is sent to the combustor for energy recovery. The treated water is suitable for recycling and is returned to the process.

The solids from distillation, the concentrated syrup from the evaporator, and biogas from anaerobic digestion are combusted in a fluidized bed combustor to produce high-pressure steam for electricity production and process heat. The majority of the process steam demand is in the pretreatment reactor and distillation areas. Generally, the process produces excess steam that is converted to electricity for use in the plant and for sale to the grid.

Since pretreatment and hydrolyzate conditioning, simultaneous saccharification and co-fermentation, enzyme production, and product recovery are the heart of the NREL's lignocellulosic biomass to ethanol process, they are described in more detail below.

Pretreatment and Hydrolyzate Conditioning

The pretreatment and hydrolyzate conditioning process area converts, by hydrolysis reactions, most of the hemicellulose portion of the feedstock to soluble sugars - primarily xylose, mannose, arabinose, and galactose. Glucan in the hemicellulose and a small portion of the cellulose are converted to glucose. This conversion is accomplished using dilute sulfuric acid and high temperature. These conditions also solubilize some of the lignin in the feedstock and “expose” the cellulose for subsequent enzymatic hydrolysis. In addition, acetic acid is liberated from the hemicellulose hydrolysis. Degradation products of pentose sugars (primarily furfural) and hexose sugars (primarily hydroxymethyl furfural (HMF)) are also formed.

Following the pretreatment reactor, the hydrolyzate liquid and solids are flash cooled, which vaporizes a large amount of water, a portion of the acetic acid, and much of the furfural and HMF. Removing these heterocyclic aldehydes is beneficial, as they can be toxic to downstream fermentation microorganisms.

In addition to flash removal of aldehydes, the acetic acid must be removed and other conditioning must be performed before fermentation. The acetic acid is removed from the liquid portion of the hydrolyzate using continuous ion exchange. After ion exchange, the liquid is “overlimed.” After ion exchange, the liquid hydrolyzate’s pH is lowered by adding sulfuric acid, then raised to pH 10 by adding lime, and held for a period of time. Neutralization and precipitation of gypsum follow the overliming step. The gypsum is filtered out and the hydrolyzate is mixed with the solids (cellulose) and dilution water before being sent to fermentation. What happens in the overliming process is not completely understood.

Saccharification and Co-Fermentation

Two different operations are performed in this process area - saccharification of the cellulose to glucose using cellulase enzymes, and fermentation of the resulting glucose and other sugars (from the dilute acid pretreatment of hemicellulose) to ethanol.

Hydrolysis, or saccharification, occurs first, separately from the fermentation. The separate saccharification step enables operation of the saccharification step at an elevated temperature to take advantage of increased enzyme activity and reduce the time and amount of enzyme required. The enzyme used to saccharify the cellulose is purchased from an enzyme manufacturer. The cellulase enzyme and diluted, detoxified hydrolyzate are continuously added to a train of five 1-million gallon vessels.

Cellulase enzyme is comprised of the following enzymes: (1) endoglucanases, which attack randomly along the cellulose fiber to reduce polymer size rapidly; (2) exoglucanases, which attack the ends of cellulose fibers, allowing it to hydrolyze highly crystalline cellulose; and (3) β-glucosidase, which hydrolyzes cellobiose to glucose. Several bacteria and fungi naturally produce these enzymes, including bacteria in ruminant and termite guts and white rot fungus. The most common organism used to produce cellulase industrially is Trichoderma reesei. Genencor International and Novozymes Biotech, the two largest enzyme manufacturers in the world, are developing more cost effective cellulase enzymes. DOE is funding this important work, which will improve the economic viability of biomass conversion.

For fermentation, the recombinant *Z. mobilis* bacterium is used as the biocatalyst. This form of *Z. mobilis* will ferment glucose and xylose to ethanol. It is assumed that mannose and galactose sugars are also fermented in this design. Several research institutions are genetically engineering strains, such as *Z. mobilis*, to utilize additional sugars, or are identifying naturally occurring organisms that metabolize hemicellulosic sugars.

The *Z. mobilis* must be “grown” in a seed fermentation train of vessels in this process area. Saccharified slurry and nutrients are combined with an initial seed inoculum (grown in the laboratory) in a very small vessel. The result of each seed batch is used as the inoculum for the next size seed increment. This series of scale-ups is continued until the last step is large enough to support the production fermentation.

Finally, the seed inoculum, nutrients, and saccharified slurry are added to a train of continuous fermenters. It is really a simultaneous saccharification and co-fermentation (SSCF) configuration at this point, because although the temperature in the fermentation tanks will be lower by necessity because of the ethanologen’s thermal tolerance, the enzyme will still continue to hydrolyze cellulose. The number of fermentors will be about five 1-million gallon vessels in a train or line. The resulting ethanol broth is collected in a beer well (storage tank) before it is pumped to distillation.

Product, Solid, and Water Recovery (Distillation, Dehydration, and Evaporation)

Distillation and molecular sieve adsorption are used to recover ethanol from the raw fermentation beer and produce 99.5 percent ethanol. Distillation is accomplished in two columns.

The first column is called the beer column which removes the dissolved CO_2 and most of the water, and the second concentrates the ethanol to a near azeotropic composition.

All the water from the nearly azeotropic mixture is removed by vapor phase molecular sieve adsorption. Regeneration of the adsorption columns requires that an ethanol water mixture be recycled to distillation for recovery.

Fermentation vents (containing mostly CO_2, but also some ethanol) as well as the beer column vent are scrubbed in a water scrubber, recovering nearly all of the ethanol. The scrubber effluent is fed to the first distillation column along with the fermentation beer.

The bottoms from the first distillation contain all the unconverted insoluble and dissolved solids. The insoluble solids are dewatered by a Pneumapress pressure filter and sent to a combustor. The liquid from the pressure filter that is not recycled is concentrated in a multiple effect evaporator using waste heat from the distillation. The concentrated syrup from the evaporator is mixed with the solids being sent to the combustor, and the evaporated condensate is used as relatively clean recycle water to the process.

Because the amount of stillage water that can be recycled is limited, an evaporator is included in the process. The total amount of the water from the pressure filter that is directly recycled is set at 25 percent. Organic salts like ammonium acetate or lactate, corn steep liquor components not utilized by the organism, or inorganic compounds in the biomass end up in this stream. Recycling too much of this material can result in levels of ionic strength and osmotic pressures that can be detrimental to the fermenting organism’s efficiency. In a typical grain-to-ethanol facility, this recycle can be limited to as little as 10 percent of the centrifuge filtrate stream to minimize this effect. For the water that is not recycled, the evaporator concentrates the dissolved solids into syrup that can be sent to the combustor, minimizing the load to wastewater treatment.

3.2.5.4 Pretreatment Technologies for Lignocellulosic Biomass

With the increasing use of lignocellulosic materials as feedstock for ethanol production, the pretreatment technologies and processes for lignocellulosic materials have received a great deal of attention recently. Physio-chemical structural and compositional factors often hinder the enzymatic digestibility of cellulose present in lignocellulosic biomass. Effective pretreatment processes become a critical step to break structural and compositional impediments to hydrolysis so as to improve the rate of enzyme hydrolysis and increase yields of fermentable sugars from cellulose or hemicellulose.

Pretreatment methods that have been most widely used include:

- Uncatalyzed steam explosion
- Liquid hot water
- pH-controlled hot water
- Flow-through liquid hot water
- Dilute acid

- Flow-through acid
- Ammonia fiber/freeze explosion (AFEX)
- Ammonia recycled percolation (ARP)
- Lime

A brief discussion of the above processes is given below.

Uncatalyzed Steam Explosion

This is a commercial process to hydrolyze hemicellulose for manufacture of fiberboard and other products. Lignocellulosic biomass is rapidly heated by high-pressure steam without addition of any chemicals. Steam can effectively opens up the particulate structure of biomass, but with little enhancement on the digestibility of cellulose in the pretreated solid.

Liquid Hot Water Pretreatment

Co-current liquid hot water pretreatment is used to pretreat corn fiber produced in the corn to ethanol process. Water pretreatment reduces the need for neutralization and conditioning chemicals since acid is not added.

Acid Pretreatment

This process has received considerable attention in both academic and industrial R&D. Dilute sulfuric acid is mixed with biomass to hydrolyze hemicellulose to xylose and other sugars and then continue to break xylose down to form furfural.

Dilute acid pretreatment has some important limitations including corrosion to the reactor. Consequently, expensive materials must be used for reactor design. The acid must be neutralized before the sugars proceed to fermentation. Formation of degradation products and release of natural biomass fermentation inhibitors are characteristics of acid pretreatment.

Lime Pretreatment

Alkali pretreatment is normally carried out at ambient conditions, but long pretreatment time is required. Unlike acid-catalyzed pretreatments, a limitation of lime pretreatment is the conversion of alkali to irrecoverable salts, or, even worse, the incorporation of salt into the biomass by the pretreatment reaction.

Ammonia Fiber/Freeze Explosion (AFEX) Pretreatment

Ammonia fiber/freeze explosion (AFEX) pretreatment method is also known as ammonia recycled percolation (ARP) process since ammonia is separated and recycled. AFEX yields optimal hydrolysis rates for pretreated lignocellulosics with near theoretical yields at low enzyme loading. Although it works only moderately well on hardwoods and is not attractive for softwoods, AFEX is well suited for herbaceous and agricultural residues.

The cost of ammonia and especially of ammonia recovery drives the cost of AFEX pretreatment process. However, the moderate temperatures and pH values of AFEX treatment minimize formation of sugar degradation products and, thus, help improve the biomass pretreatment economics. In addition, residual ammonia is a needed fermentation nutrient.

3.2.6 Biomethane

3.2.6.1 Biodigestors

Overview

Anaerobic biodigestion, though not itself a liquid biofuels process, can be an important enabling technology for certain biofuels projects. It is applicable to liquid biofuels process and project development in several ways:

- To convert the by-products or co-products of biofuels processes to more readily usable energy to support the biofuels production facilities
- To serve as an alternative to the perhaps more difficult, but more compact process of thermal gasification of biomass
- To supplement these by-product resources, if required and/or if economically attractive, by converting a wide range of extraneous biomaterial resources, especially some problematic industrial, agricultural, or municipal wastes that have negative value, that is, yield a “tipping fee”, or disposal charge, that enhance the economics of a project
- To produce biosyngas for further chemical conversion by steam reforming of the methane contained; biosyngas can be used to make:
    - Various additional liquid biofuels by catalytic synthesis
    - Hydrogen for hydrogenation steps integral to a number of the production processes considered in this report, such as methyltetrahydrofuran (MTHF) from levulinic acid for P-Series fuel, two-step *n*-butanol production from fermentation butyric acid, etc.

Modeling of some of these concepts is discussed in greater detail below.

This technology is also covered as part of the overall process for lignocellulosic biomass fermentation to fuel ethanol modeled above. There, it is used to digest a stream of unconverted C_5 sugars and other soluble and suspended fermentation residuals to methane-containing low-Btu fuel gas that is combusted in a power island along with lignin and other residuals to generate power for the facility and for sale to the grid.

Anaerobic digestion is not new to waste management or energy production. Reportedly, it was first attempted to collect and utilize methane gas produced from wastewater treatment in an anaerobic septic tank in 1885 in Exeter, England, where the methane served nearby gaslights. Over the past 50 years, anaerobic digestion has been used extensively in North America to treat biosolids, comprised of primary and biopond residual sludge, though the capture and utilization of methane has not typically been part of that process, except at larger wastewater treatment facilities, where the costs of gas engines (or more recently, fuel cells in some cases) are justified.

In Europe, however, there is more experience with energy utilization by heat and power generation in farm systems as well as in municipal and industrial ones.

Today, biodigestion is commonly practiced in a wide range of important industrial and public sectors in North America, Latin America, Europe, Asia, and elsewhere:

- Manure disposal/utilization for cattle feedlots, dairy farms, and piggeries
- Food processing liquid wastes, including from dairy factories, slaughterhouses and meat packing, poultry processing, fish processing, vegetable and fruit packing, prepared foods, starch processes, winemaking and other beverage operations
- Disposal of municipal solid waste (MSW) and industrial waste stream organic fractions (post-consumer food, paper, yard waste, etc.)
- Leachate from landfills
- Biosolids (primary and post-treatment sludge) treatment in publicly owned treatment works (POTWs) and industrial biopond
- Paper industry wastes – from both primary and recycle pulping
- Vinasse from sugarcane ethanol production in Latin America and India

There are also aerobic (air blown) processes sometimes used as secondary treatments to reduce the odors or toxicity of the solids residues from anaerobic biodigestion, and sometimes as the only treatment, simply to efficiently dispose of the solids. The most advanced and effective are known as ATAD (aerobic thermophilic autothermal digestion). These reduce the volume of the biosolids contained, some of which may be refractory to anaerobic processing, but they produce no methane.

Basic Process

Anaerobic biodigestion is the process of enzymatically converting wet biological solids (biosolids) to methane-CO_2 mixtures (“biogas”). Methane gas (CH_4) is the major component of natural gas. Natural gas is a fossil fuel whose origin, at least in some of its sources, is probably biogenic, that is, created millions of years ago by the anaerobic decomposition of organic materials. Methane that is often found in association with coal and petroleum is probably biogenic. Other methane resources may be non-biogenic, since methane is found throughout the universe in places where it is likely life never existed. Anaerobic bacteria are some of the oldest forms of life on earth. They break down or "digest" organic material in the absence of oxygen and produce biogas as a waste product. (In contrast, aerobic decomposition, or composting, requires large amounts of oxygen and produces heat).

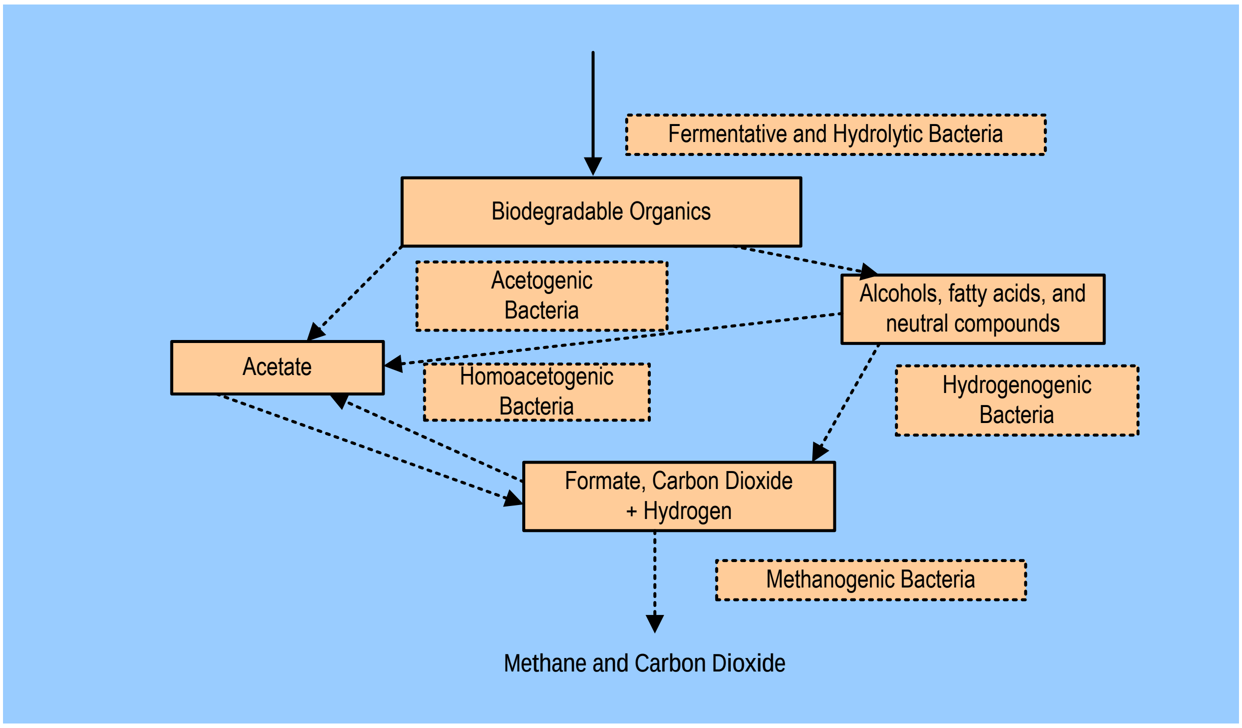
Anaerobic digestion is actually a complex process that involves several basic stages employing a variety of microorganisms. Thus, the complex organics in animal wastes and other types of wastes commonly treated (including sugars and other carbohydrates, fats, and proteins) produce a roughly equi-molar mixture of methane gas and CO_2 through the action of four main microbial cultures that work together to break down the waste, producing fatty acids that are further broken down to produce methane:

- Initially, a group of fermentative and hydrolytic microorganisms converts organic material to more digestible forms, such as sugars

- A second group, acetogenic organisms, uses these materials to generate fatty acids, other organic acids, and acetate
- Homoacetogenic and hydrogenogenic organisms reduce these compounds to even simpler compounds - formate, carbon dioxide and hydrogen
- Methanogenic (methane-producing) anaerobic bacteria complete the decomposition process

In this fermentation process, as shown in Figure 3.18, the two final steps metabolize 70 percent of the methane from acetate and 30 percent from carbon dioxide reduction with hydrogen. Anaerobic digestion can effectively treat a variety of wastes and produce methane.

Figure 3.18 Biodigestion Fermentation Metabolic Pathway



Source: Barole, A, et. Al, ORNL, 2006, D. Palmer, Agrisa, and Nexant

Several factors affect the rate of digestion and biogas production, the most important of which is temperature. Anaerobic bacteria can tolerate temperatures ranging from below freezing to above 135°F (57.2°C), but they thrive at temperatures starting around the same as human body temperature, about 98°F (36.7°C) (mesophilic) and up to 130°F (54.4 °C) (thermophilic). Under normal anaerobic conditions the bacterial activity, and thus biogas production, falls off sharply between about 103°F and 125°F (39.4°C and 51.7°C), and more gradually from 95°F to 32°F (35-0°C).

Decomposition and biogas production occur more rapidly in the thermophilic range than in the mesophilic range. "Extremophiles" (microbes that thrive at higher temperatures and/or under more aggressive conditions of pH or chemistry) are being systematically sought by researchers.

Some of these, with or without genetic modification, might extend this temperature range and allow faster and more complete conversions at higher temperatures.

The biodigestion process is highly sensitive to disturbances, such as changes in feed materials or temperature. While all anaerobic digesters reduce the viability of weed seeds and disease-producing (pathogenic) organisms, the higher temperatures of thermophilic digestion result in more complete destruction of such problematic life forms. Although digesters operated in the mesophilic range must be larger (to accommodate a longer period of decomposition, or residence time, within the digestion tank), the process at these temperatures is less sensitive to upset or change in operating regimen.

In most climate regimes in the United States, biodigester vessels require some insulation and/or heating. Some facilities circulate heat recovered from their biogas-powered engines in or around the biodigester, while others burn part of the biogas to heat the biodigester. In a properly designed system, heating generally results in an increase in biogas production during colder periods. Systems to convert manure are typically free-standing and self-contained. The process is complex, and while studies on digesters in the north-central United States indicate that maximum net biogas production can occur in digesters maintained at temperatures as low as 72°F (22.2°C), in general maintaining higher temperatures is optimal. In facilities integrated with biofuels production, opportunities will likely abound to exploit process waste heat in the range of 100-130°F, and thereby avoid burning biogas.

Other factors affect the rate and amount of biogas output, including pH, water/solids ratio, carbon/nitrogen ratio, mixing of the digesting material, the particle size of the material being digested, and retention time. Pre-sizing and mixing of the feed material for a uniform consistency allows the bacteria to work more quickly. The pH is self-regulating in most cases. Inexpensive buffers such as bicarbonate of soda can be added to maintain consistent pH. It may be necessary to add water if the feed material is too dry or if the nitrogen content is very high. A carbon/nitrogen ratio of 20/1 to 30/1 appears to be optimal. Mixing or agitation of the digesting material can aid the digestion process. Antibiotics in livestock feed have been known to kill the anaerobic bacteria in digesters.

Process Configurations

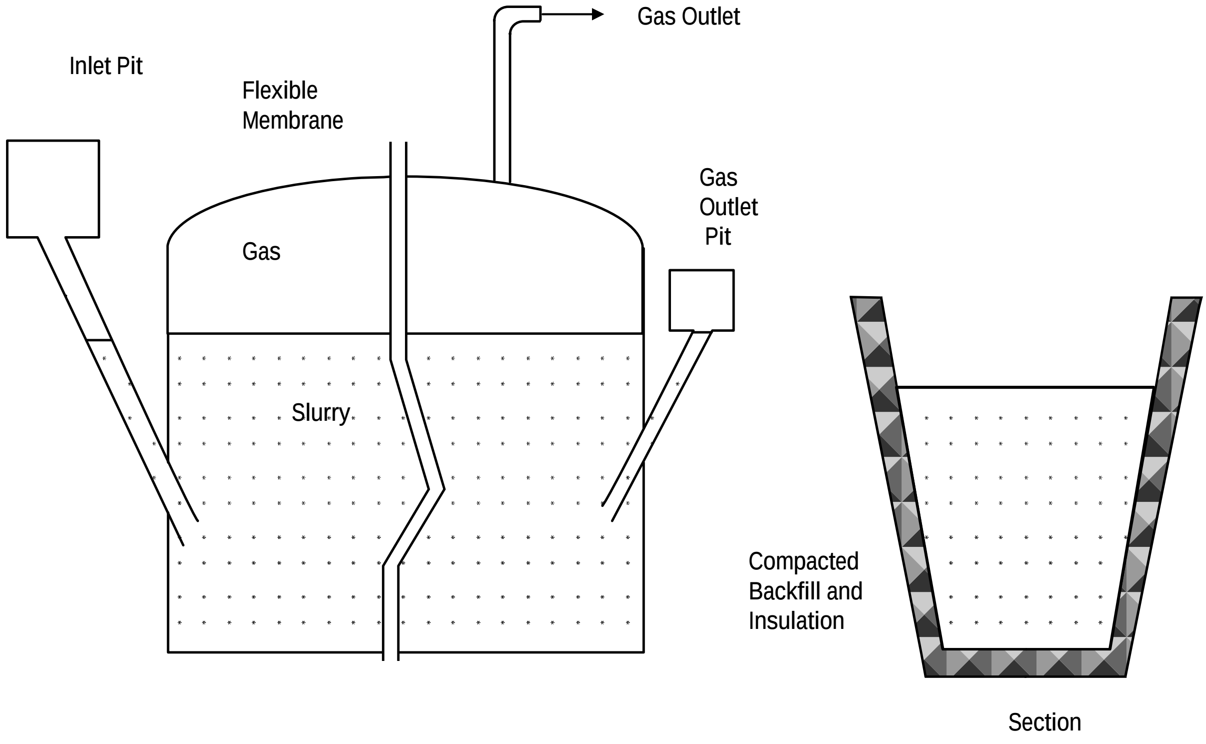
A biodigester is the central structure of a biogas plant. It is generally an air and water-tight chamber that provides anaerobic conditions for the various chemical and microbiological reactions described above. It can be made of various construction materials and in different shapes and sizes, based on external parameters, such as limits on capital outlay, treatment efficiency and net energy yield goals, and operational skill. The technology available ranges from very rudimentary to sophisticated, and from family farm to full commercial scale. Anaerobic digesters are sometimes contained in earthworks, but often are vessels (in most cases large, cylindrical, covered tanks) designed to retain decomposing manure for sufficient time at the design temperature to allow the growth of methanogenic bacteria in a steady-state. Electricity and heat production with the generated methane are direct benefits of anaerobic digestion. The digested solid effluent has an earthy smell with some ammonia present, and can be utilized in various ways, depending on its quality. It often needs some type of further treatment, usually involving aeration, to be of maximum value.

The following is a summary of the main types of digesters commonly used in the agricultural sector, excluding the more primitive or smaller-scale ones (e.g., bag-type used by family farms):

- Plug-Flow Digesters

These have a simple design of a trough and a slurry digester vessel, pictured in Figure 3.19. The dimensions are typically 1:5 (channel width to length), and the total size is determined by the rate of feed. An expandable cover collects the biogas. The hydraulic retention time (HRT) is typically 20–30 days, and the solids concentration is typically 11–13 percent. Plug-flow digesters are sensitive to the amount of solids in the feed, since the feeding of the solids at one-end drives the contents towards the other end.

Figure 3.19 Schematic of a Plug-Flow Digester



Source: Renewable Energy Sources and Technologies on Farm Systems, The Royal Veterinary and Agricultural University, Denmark, 2004

- Complete-Mix Digesters

These digesters have internal mixing and are usually similar to a chemical reactor – tall, circular, heated, with good controls. They have relatively high capital and maintenance costs. Sizes typically range from 95 thousand to 1.9 million liters (25-50 thousand gallons). The solids concentration range is 3-10 percent and the HRT is 10-20 days.

- Slurry Digesters

Slurry digesters operate in the same solids regime as the plug-flow and complete-mix digesters. They require no mechanical mixing and are often constructed in silo configurations where internal convection (from temperature gradients and gas evolution) provides mixing.

- Covered Lagoon Digesters

Lagoon digesters are used to treat streams with low solids concentration (less than 3 percent). This is a popular method for methane production where manure removal from the livestock operation is by flushing, generating large volumes of low-solid waste. The HRT is about 60 days, implying that the conversion rate is very slow. One or more years may be required to reach steady-state conditions in the lagoon. A floating cover collects the methane. The cost of these digesters is low and they are not heated, making methane production very dependent on the weather conditions.

- Anaerobic Filter

This type of digester was developed in the 1950s to reduce reactor volumes in processing relatively dilute and soluble wastewaters with low levels of suspended solids. It features a reactor in the form of a column filled with a non-biodegradable packing medium, such as stones, plastic packing, shells, reeds, and wood or bamboo shapes. There are a number of technology offerings in this area by vendors of structured and random contactor packing systems. Expanded-bed reactors that use sand or granular activated carbon as a substrate on which bacteria can live are a related design.

- Attached Film Anaerobic Digestion (AFAD)

The filter and expanded-bed concepts were extended further in the development of the AFAD expanded-bed reactor in 1980. In this process, waste flows upward through bacteria attached to a bed of suspended media, which are generally more monolithic, such as vertically suspended PVC tubes, fiber media, etc. This design is related to the baffled reactor and the upflow anaerobic sludge blanket (UASB), which are both described later in this section. The system modeled by Nexant for this report is of this general type.

Immobilizing bacteria as a biofilm avoids washout of slower growing cells and allows biomass retention that is independent of residence time, increasing biomass development. A larger population of bacteria per unit reactor volume reduces reaction time. Retention time in these systems ranges from 2-6 days, versus 10-20 days for the more common complex-mix systems.

This process is ideal for large volumes of dilute, low-strength wastewater (<1 percent solids), such as those generated from dairy farms and some biofuels plants. Fixed film digesters have a smaller footprint, which is more important in a process plant context. These systems are also able to start up faster than suspended growth systems. They can be more successful because of the inherent preference for bacterial species to live in an attached growth mode versus a suspended growth system. There is continual research on engineering better surfaces on which the bacteria can live.

A unique version is offered by Ecovation, Inc. (Victor, N.Y.) in a patented technology that it describes as an ultra high-rate, anaerobic treatment process, called Mobilized Film Technology (MFT). This has a number of installations at food processing and other wastewater facilities. Ecovation claims that MFT improves on the expanded and fluidized bed technologies, and results in an optimal system for removing organic material from what they describe as high-strength wastewater (up to 10 thousand mg per liter, or 1 percent, total dissolved solids [TSS] and up to 500 mg per liter of fats, oils, and grease [FOG]). Despite its name, the technology uses immobilization of bacterial thin films on heavy, small diameter inert particles, which are indeed, free to move about (be mobile) when agitated. MFT uses a special nozzle design to inject wastewater with suspended solids being treated into a settled bed of these coated inert particles, and thus agitate and mix the two systems for contacting. The treated organics float upward and the coated inert particles settle out within the chamber. The material being treated overflows the chamber (zone) to be pumped to the next zone. This is illustrated schematically in Figure 3.20.

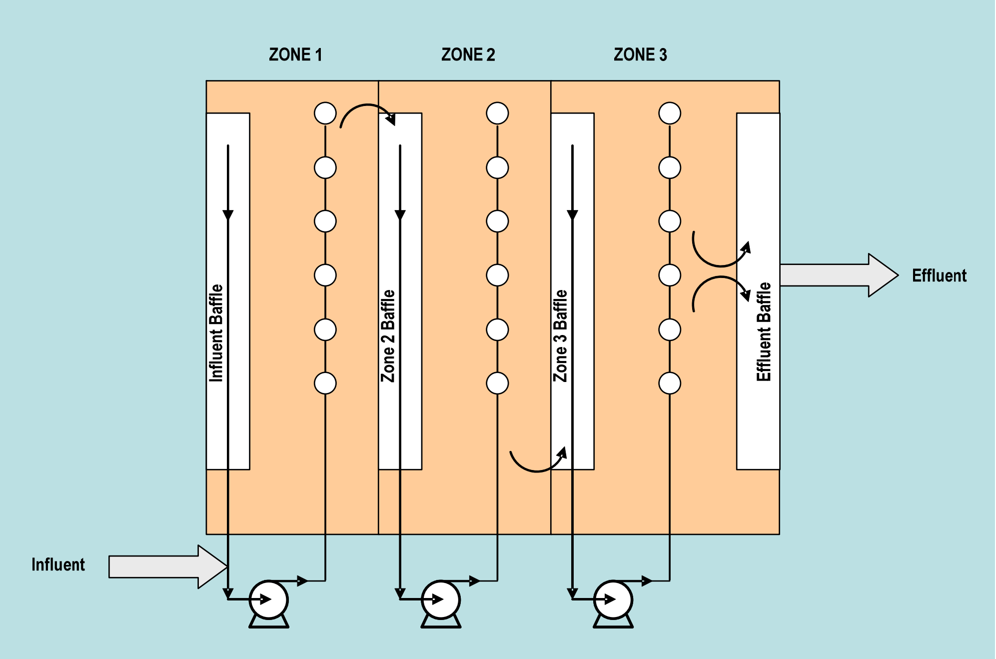
- Anaerobic Baffled Reactor

This design, pictured in Figure 3.21, was developed by Bachmann et al. (1982) at Stanford University, CA and it works well with dilute as well as more concentrated feeds. The reactor is a rectangular tank divided by vertical baffles into five or six equal compartments, in which the liquid flows alternately upward and downward between the baffles, and on its upward passage the waste flows through an anaerobic sludge blanket at the bottom of the tank. Hence the waste is in intimate contact with active and stable biomass, but due to the design, a large inventory of biomass is retained in the reactor.

- Anaerobic Contact Digester

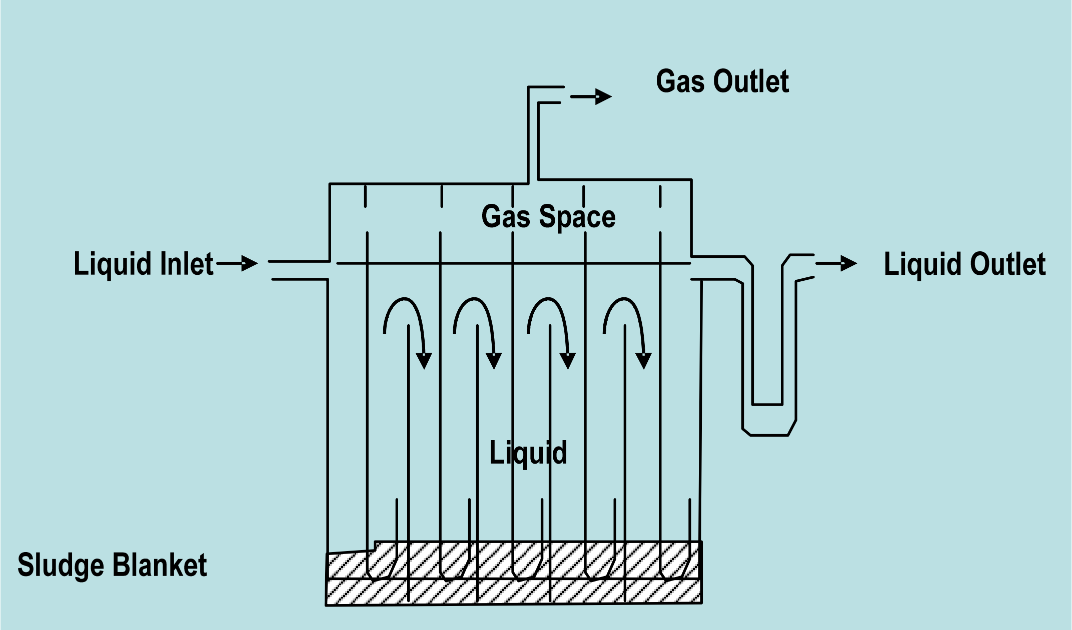
This type of design, pictured in Figure 3.22 was first used in 1955 in Europe. In it, the sludge microorganisms are separated by sedimentation or mechanically-enhanced means and are returned to the digester to provide stabilization for the reaction regime. A key issue with this system is that the anaerobic sludge continues to produce gas as it leaves the digester, thus, it is frothy, leading to problems in getting it to settle in a reasonable time. Various methods have been used to mitigate this problem, including thermally shocking the effluent, and vacuum degasification. Some large-scale plants are currently operating in developed economies.

Figure 3.20 Ecovation Plug Flow Schematic



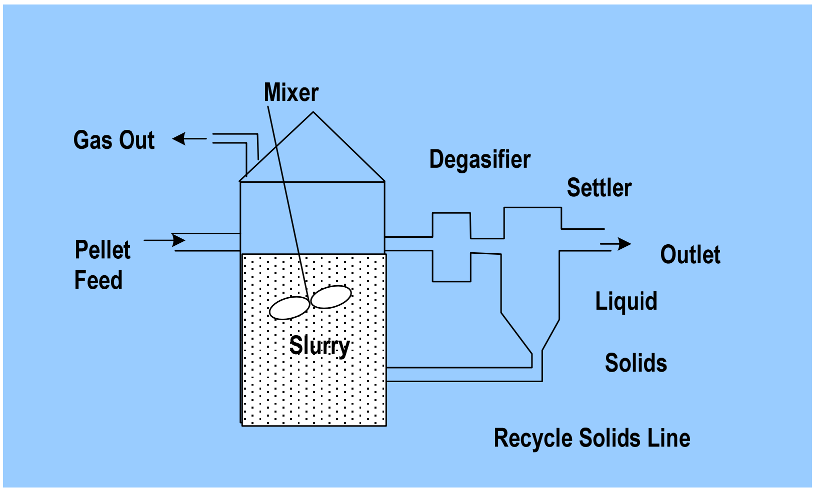
Source: Ecovation, Inc., 2009

Figure 3.21 Anaerobic Baffled Reactor



Source: Bachmann et al., 1982

Figure 3.22 Anaerobic Contact Digester



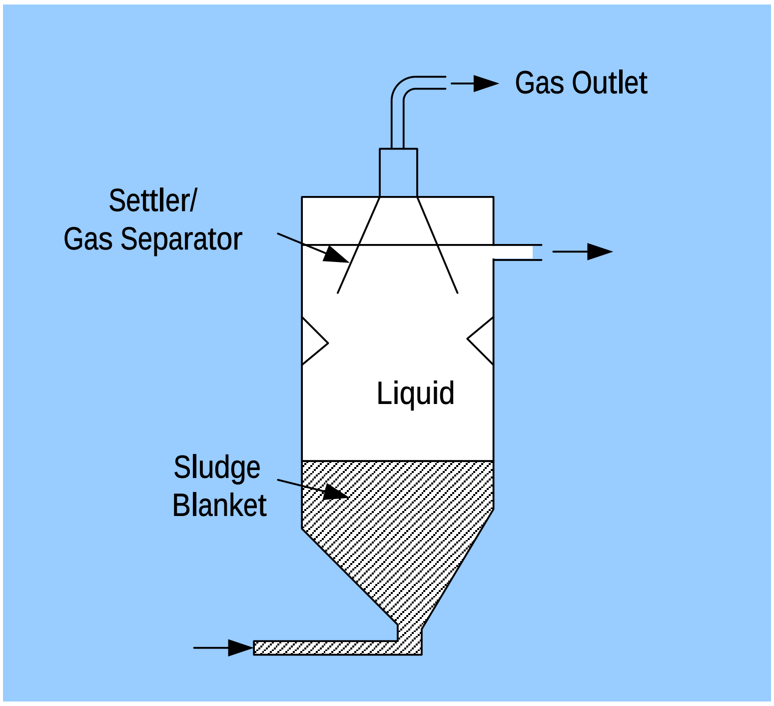
Source: Renewable Energy Sources and Technologies on Farm Systems, The Royal Veterinary and Agricultural University, Denmark, 2004

- Upflow Anaerobic Sludge Blanket (UASB)

This design, pictured in Figure 3.23 was developed in the Netherlands in the 1980s. The digester is in the form of a rather complex circular tank in which the processed material enters a conical bottom and flows upward through an anaerobic sludge blanket. Solid/liquid separation is achieved by the effluent exiting through an inverted cone at the top of the digester. Operating this system requires a relatively high degree of sophistication, especially during the critical startup period, or following any upset.

The UASB process has been improved since its development in the 1980s. In recent years, UASB utilizing granular technology has been applied to enhance concentration of sludge or bacteria to improve efficiency of the reactor. UASB uses an anaerobic process that forms a fine granular sludge blanket that acts as a filter to prevent the solids in the incoming wastes to flow through as the liquid part does. Wastewater flows upwards through the blanket and is processed by the anaerobic microorganisms. The upward flow combined with the settling action of gravity suspends the blanket with the aid of flocculants. In about 3 months the blanket reaches maturity and small sludge granules begin to form. The blanket’s surface area is covered in aggregations of bacteria that create a selective environment in which only those microorganisms, capable of attaching to each other, survive and proliferate. The concentration of sludge and bacteria allow for higher flows in the biodigester and therefore more wastewater can be treated by the concentrated anaerobic microorganisms. The process has now become well established and is used world wide for waste water treatment.

Figure 3.23 Upflow Anaerobic Sludge Blanket (UASB)



Source: Renewable Energy Sources and Technologies on Farm Systems, The Royal Veterinary and Agricultural University, Denmark, 2004

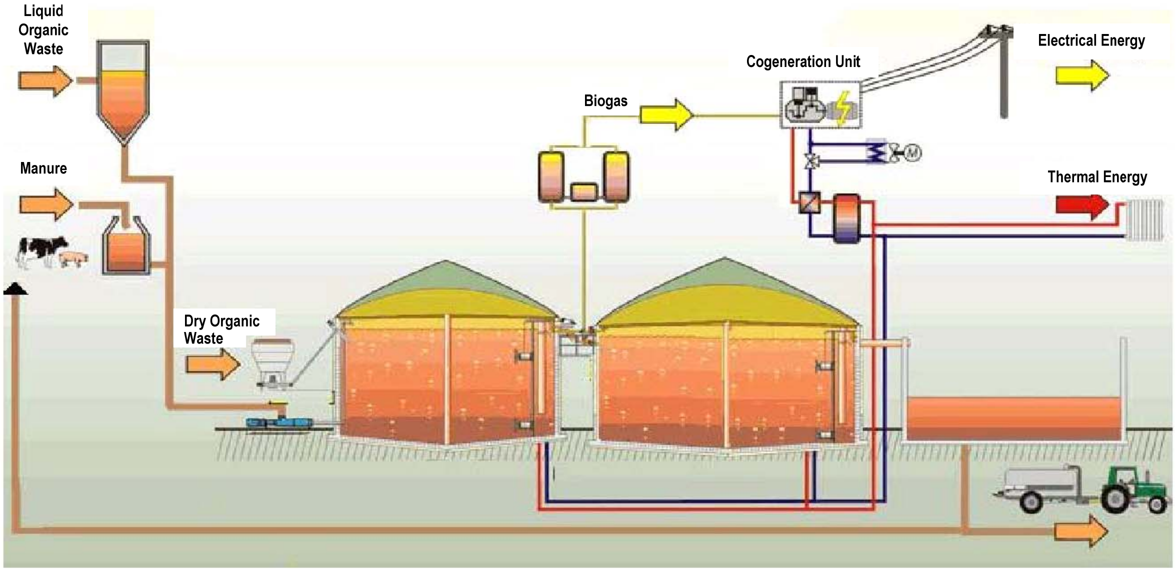
- Staging

Anaerobic biodigestion systems can also be classified by number of stages:

- In single-stage systems, the oldest and most common approach, both types of microbiological processes occur in the same vessel or stage
- Two-stage systems provide a separate reactor for each biological activity (e.g., one reactor for hydrolysis and acidification and one for methanogenesis). A relatively recent development in anaerobic digestion, two-stage systems involve two reactors, each designed to optimize the process dynamics of the different stages of anaerobic digestion (e.g., acid formation and gas formation)
- Standard Engineering Systems

Biodigestion systems offered by Biogas Energy Inc. (Seattle, WA), using reactors that can be described as the complex mix type listed above, appear to be good examples of the state of the art units integrated with liquid biofuels plants. Their design approach, consistent with that of other designers of similar systems, is abstracted. The process is illustrated in Figure 3.24.

Figure 3.24 Typical Farm-based Biodigestion with Energy Production



Source: Biogas Energy Inc., 2008

Substrate Feed

Manure is pumped from a receiving tank into the digesters. Since livestock extract much of the biodegradable materials in their feed, manure has low energy content, so to generate significantly more methane than with manure alone. Digesters can be fed multiple substrates, including possibly: residuals from fermentation ethanol production, wastes from transesterification as well as crude glycerol, grease, ground corn stover, food processing waste, ground organics fraction of MSW, or post-consumer food waste. Manure produces biogas at 25 m³ per ton, corn silage at 190 m³ per ton, and grease at 961 m³ per ton.

Continuous mixing in the digesters maintains an optimal environment for bacteria to digest these additional high-energy materials. A pump or screw conveyor feeds the dry raw materials into the digesters. Automated feeding, as appropriate, regulates a constant ratio of materials fed to ensure optimal digestion and reduce operating labor requirements.

Digesters

Biogas facilities will typically have two or more cylindrical, reinforced-concrete digesters with heating pipes embedded in the walls and floor. These are typically concrete tanks, which are cost-effective and have a long operating lifespan. The walls are insulated and clad with weatherproof panels, unless in a tropical location. The digesters are above-ground structures to reduce costs and facilitate maintenance. Having two or more digesters in series provides several crucial benefits over a single tank design:

- Redundancy: If one digester is taken offline, the other continues to operate without interruption, so that manure and other feeds do not back-up in inventory. The first digester typically generates approximately 80 percent of the total methane and kills approximately 96-98 percent of pathogens. The second digester produces the 15-20 percent additional methane and kills 96-98 percent of any pathogens surviving the first reactor, leaving a minimal pathogen survival rate

- Pathogen treatment: It should also be noted that pathogen treatment can be augmented by pasteurizing the substrate before it is digested, using surplus heat generated by the combined heat and power (CHP) unit
- Expansion: Facility capacity can be increased by adding digesters
- Disaster prevention and rapid recovery: If the bacteria in one digester become contaminated or poisoned, healthy inoculate from the other digester can be added to restore it quickly. Digesters are connected to each other, so substrate can be directed from a "healthy" digester to a "sick" one

Other digester types, such as plug flow, modified plug flow, lagoon, or single tank continuous mix do not have distinct phases and therefore are not as efficient in energy production or pathogen treatment.

Roofing System

Digesters are covered with double-membrane roofs to protect them from the elements, to allow easy access to the contents, and to provide built-in gas storage. In one case, a roof's outer membrane has withstood harsh Northern winter climates for over a decade, while the inner membrane expands and contracts as a built-in gas holder for up to 10 hours of biogas production. An air pump maintains pressure between the two membranes, providing the outer membrane stability while applying pressure to the inner gas storage.

Gas storage as standard equipment provides cost savings and energy production efficiencies. For example, when the combined heat and power unit is turned off for routine maintenance, the gas can be stored until operations resume - no methane is lost to flaring. The CHP unit can be turned down overnight to build up a gas reserve and then run at maximum capacity during peak rate hours. If problems develop within a well-engineered flexible roof digester, the roof can be unhitched and folded back to give instant access. This would be impossible with a steel or concrete roof. This keeps downtime to a minimum.

Mixing

The contents of each tank are mixed with 2-4 submerged agitators to promote optimal bacterial proliferation and ensure steady, reliable methane production. The agitators adjust automatically or manually. Agitators have an expected lifespan of 8-10 years since they only run an average of 5 minutes each hour. Repair or replacement is simple, and replacements can be put in place in minutes.

Desulfurization

High levels of H_2S reaching the CHP unit cause severe degradation of the machinery and mechanical failures. Desulfurization systems in the digesters reduce hydrogen sulfide levels to 100-250 ppm depending on substrates.

CHP Unit

Following desulfurization, the biogas is converted into electrical and thermal energy in a CHP, or cogeneration unit. All of the facility's loads, including the digester heating, run on power generated by the CHP unit. Surplus electricity (typically 95 percent of the amount generated) is sold to power utilities through the grid. Additional heat can be used to heat homes or buildings as well as for on-site agricultural and industrial processes that require significant heat.

Monitors and Controls

Digesters can be provided with a biogas analyzer that continuously monitors CH_4, CO_2, and H_2S, and can be checked remotely by computer. Any changes in the biogas composition can be quickly detected to prompt the appropriate action, i.e., adjusting agitators, adding buffer materials, etc. Quick response time means better methane production and disaster prevention. The biogas analyzer is also used to optimize the biocatalytic gas cleaning system. Ph meters can also be installed.

Manual Adjustments

Facilities are typically built with a working platform and viewing windows to set the mixing devices at optimum positions and for early detection of process-related biological changes inside the digester (e.g., formation of foam or crust).

- Non-Agricultural (Solid Waste) Systems

Wet Systems

Non-agricultural digesters include designs that are not commercialized for farm use, such as UASB reactors and sequencing batch reactors used for industrial and municipal solid waste treatments. These types have potential for faster processing rates, but rely on more complex designs and thus higher capital and operational costs. Wet systems processing MSW and sewage sludge use a relatively higher percentage of solids than farm systems to produce a substrate with 10-15 percent total solids (TS).

BTA and Wassa are two examples of wet processing technology used for MSW. More than 26 facilities have been built using the BTA technology in Europe since the 1980s. The BTA process can be designed in a single train to treat 110-550 tons per day of solids, and typically produces over 75 kWh per ton of feed. Such plants would have capex of $23 million to $33 million, respectively.

Dry Systems

Dry systems mix the incoming solid waste with a relatively small amount of water. In many cases, the substrate is mixed to produce 15-40 percent total solids. Examples of commercially available dry systems include Dranco, Kompogas, and Valorga.

According to industry analysts, there are approximately 150 anaerobic digestion plants around the world that process a variety of semi-solid waste streams, and 45-50 different manufacturers of digestion equipment. Most process agricultural or industrial wastes or sewage sludge, and fewer plants in the United States or Canada process MSW or sewage sludge. Though Europe has a lead in this area, it also has few MSW-based biodigesters.

A brief overview of the MSW anaerobic digestion technologies, including wet and dry and one and two-stage systems, which might also apply to integrated biofuels plants, is provided in Table 3.8.

Table 3.8 Summary of Leading MSW Biodigestion Technologies

Technology	Example	Advantages	Disadvantages
One-Stage Wet Processing	Wassa Technology	Known Technology	Potential for 15-25 percent loss in biomass yield when processing mixed waste
	Wassa, Finland BTA Dufferin plant, Toronto, Canada	Relatively low equipment cost	
One-Stage Dry Processing	Dranco	Less pretreatment compared to wet systems	Requires expensive reactor loading equipment (e.g., conveyors, screws and pumps) compared to wet systems
	Valorga	Small reactors	Drier feed stream is harder on equipment
	Kompogas	Superior pathogen destruction	
		Low reactor heat requirement	
		Low rate of water consumption and discharge compared to wet systems	
Two-Stage AD Systems	BTA larger plants (wet)	Design flexibility	Complex and not widely tested
	Subbor Guelph (dry)	Potentially more reliable for waste that degrades quickly (e.g. kitchen waste)	Higher capital cost
		Lower heavy metal concentrations in compost	

Though biogas yields compare favorably with wet systems, they could be potentially higher because heavy material at the bottom of the tank or top layer foam are not removed before complete digestion. Capital costs for both systems are comparable, even though dry systems require more durable and thus more expensive loading and handling equipment compared to wet systems that pump highly diluted slurry into the reactor through a relatively simple centrifugal pump. However, the higher capital cost of handling equipment is partially offset by a relatively simple pretreatment process that is less extensive than that required by a wet system (e.g., metal and stone removal, shredding, etc.). The capital cost of a dry system reactor could be lower than that for a wet system because the volume to be handled is less than in a dry system reactor due to a lower dilution rate. Dry systems consume and discharge significantly less water than wet systems. Depending on the dry system technology, there is potential to utilize thermophilic temperatures that can result in a greater rate of pathogen destruction.

Economics and Integration

- Overview

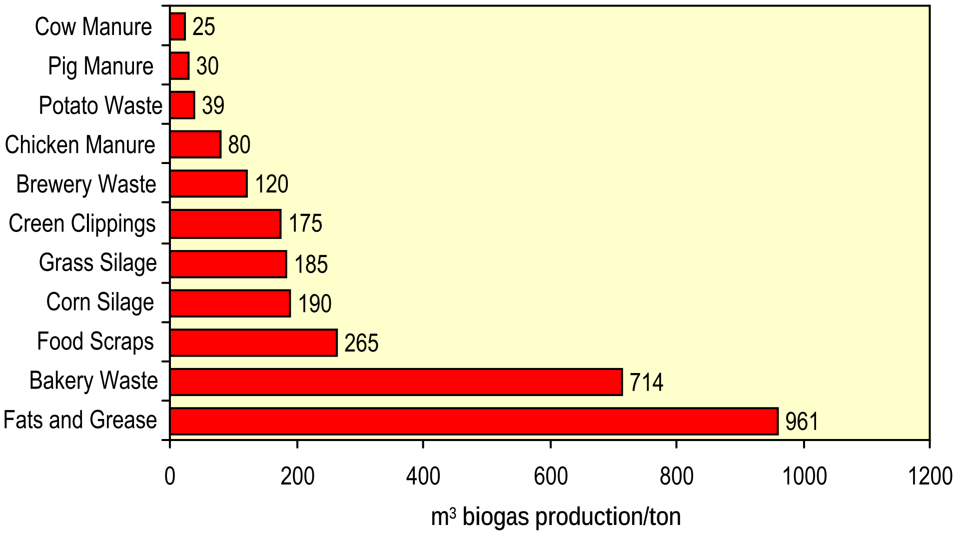
As mentioned above, anaerobic digestion is more extensively used outside of the United States, where treatment of animal waste has been a concern for a longer time. In Germany, with more than two thousand anaerobic digesters operating, biogas production has undergone decades of continual quality improvement. Since German farmers purchase digesters primarily for energy production, they demand the highest efficiencies. Since they operate their digesters themselves, low-cost maintenance and operation is crucial.

In the United States, the first dairy waste digesters were installed principally to produce energy during the mid-1970s energy crisis. The first pig manure digester systems in the United States were installed principally to control manure odors. Larger animal production units, including vast CAFOs (Confined Animal Feeding Operations), or feedlots, and recognition of the pollution potential of these farms have resulted in greater regulation in the United States. The new rules and guidelines make manure treatment a larger expense in modern farming. Farmer motivation for building and operating anaerobic digesters has expanded from direct energy benefits to include key non-energy benefits such as: odor control, improved manure handling, mineralization of organic nitrogen, weed seed destruction, pathogen reduction, and by-product production such as digested dairy solids.

- Mixed Feeds

Superior methane production can be achieved by adding other substrates to manure. In addition, various substrates have different methane production capacity, as shown in Figure 3.25. Plug flow and covered lagoon digesters are unable to efficiently digest these materials. In addition to increased methane production, multiple substrates provide waste disposal tipping fees.

Figure 3.25 Typical Biogas Yields from Various Bio-Wastes



Source: Biogas Energy Systems, 2008

Therefore, to enhance the technical and economic viability of biodigestion, it appears that combining feedstocks and operating with higher solids feeds may be key. This might mean processing feedlot manure together with agricultural field wastes and processing residuals from a biofuels operation. Experience with MSW treatment and biodigestion could be relevant to this strategy.

Case Studies – Proposed Ethanol-Feedlot-Methane Systems

- E3 Biofuels Complex

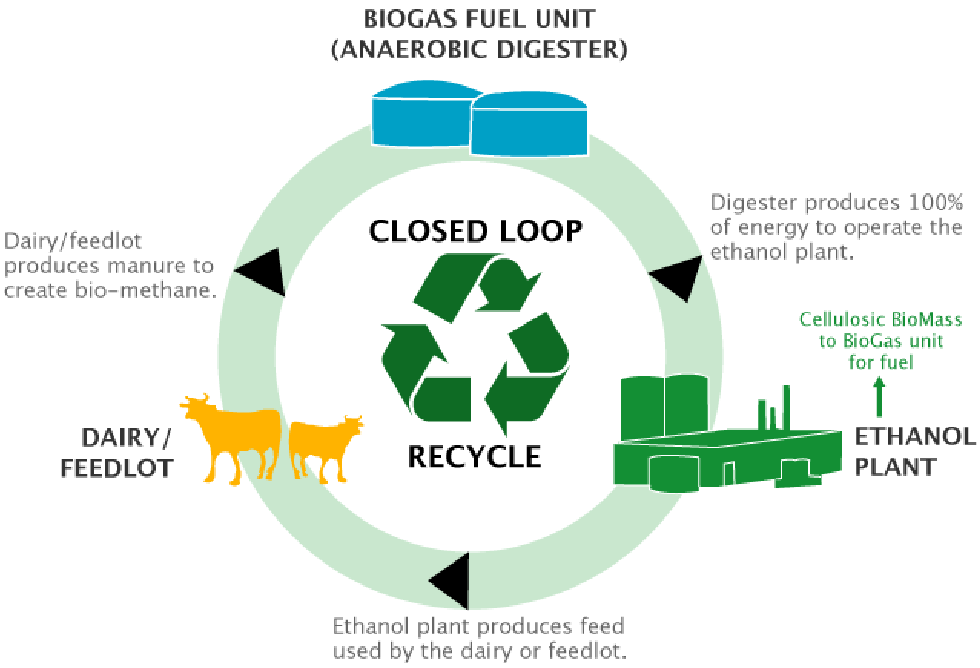
The E3 BioFuels Complex in Mead, NB, is a new self-sustaining, closed-loop system that combines ethanol production, feedlot livestock production (a concentrated animal feeding operation, or CAFO) and/or dairy production, and waste management in an anaerobic digester. It is reported to be in the final stages of development with operations beginning in December, 2006. The manure from the livestock will be handled by an on-site biodigester to produce biogas. The biogas will power the ethanol production process, eliminating fossil fuel costs. Fermentation residuals from dry corn mill ethanol production would be used as enriched cattle feed in the form of wet distillers grains and solubles (WDGS) that could replace more than 40 percent of the corn feed presently used, completing the loop. The Mead Cattle Company's adjacent feedlot of 30 thousand head of cattle will thus be integrated with production of approximately 24 million gallons of fuel ethanol annually. Similar systems exist elsewhere in the United States, such as at an Abengoa ethanol plant in New Mexico, which sells their grain milo fermentation WDGS to adjacent feedlots. The WDGS feed mixture is expected to increase cattle growth rates and reduce the use of hormones and antibiotics in the feed ration, while producing a higher quality beef.

The ethanol plant will process more than 8 million bushels of corn annually and produce 100 thousand tons of WDGS. Feeding the wet grains to cattle on-site avoids the energy-intensive drying of WDGS to make DDGS (distillers dry grains and solubles), which is otherwise needed to preserve this substantial by-product (1:1 with ethanol) for shipment. This will lead to substantial savings in plant capital, operating costs, and energy costs for the integrated facility.

Using biogas for power and heat in the facility also eliminates the second largest cash cost component of many dry mill corn fuel ethanol plants today - natural gas purchases. This and the overall approach of on-site WDGS feeding makes plant location decisions more independent of rail and gas pipeline access.

The process is illustrated in Figure 3.26.

Figure 3.26 E3 Closed Loop Ethanol Production, Beef/Dairy and Waste Management



Source: E3 Biofuels LLC, 2009

Table 3.9 summarizes milestones for this project.

Table 3.9 E3 Biofuels Complex Project Milestones

Patent issued for E3 BioSolution technology	March 2002
Construction begins on E3 Mead complex:	September 2005
Construction time for E3 Mead complex	8-11 months
Effective date of new EPA regulations governing CAFOs:	January 2007

- PRIME

A similar project was reported to be under development in 2003 in South Dakota by PRIME (Pierre Renewable Integrated Meat & Energy) Technologies, LLC, aimed at integrating an enclosed custom cattle feedlot, an anaerobic digester, and a modified ethanol unit. The $50 million project would be located in Sully County, 15 miles north of Pierre, South Dakota, and would be one of the largest new operations of its kind in the state and in the United States. Following a feasibility study, federal and state funding was reported in 2003 to have been confirmed to proceed to the next phase of development, but no further progress is apparent in the public record.

Like the Mead, NB project, the PRIME complex was to be a closed-loop system to produce beef, fuel ethanol, and methane, as well as biochemical fertilizers. Each of the component technologies proposed appears to be well proven on a standalone basis, but none had previously been combined to capture economies of scale through process integration. The project was to consist of a 15 million gallon per year fuel ethanol plant, an adjoining feedlot containing 25 thousand head of cattle with a closed manure collection system, and an anaerobic digester. The anaerobic digester would produce methane for the ethanol plant and biochemical fertilizers for use by farmers.

Other expected system benefits included a reduction in environmental pollutants such as biochemical oxygen demand (BOD), pathogens, methane, ammonia, and nitrous oxide (N_2O) emissions. Nutrient pollution would decrease because nutrients would be captured as organic biochemical fertilizers. Preliminary estimates indicated that 16 percent less corn would be required by the integrated complex, which was projected to increase ethanol conversion efficiency from 2.6 gallons per bushel of corn to 3.1 gallons per bushel.

The design of the complex was reported to also allow the use of emerging ethanol production technologies that convert the hemicellulosic fraction of agricultural residues (e.g., corn stover) into five-carbon sugars that can be converted to ethanol when economically feasible to do so.

The developer envisioned that marketing carbon credits would potentially have provided further protection in times of economic stress. The anaerobic digester would replace traditional animal waste storage tanks and lagoons, a major cause of pollution and feedlot odor in the region. It was projected that the biogas would contain approximately 60-70 percent methane to be used to meet the majority of the ethanol plant’s internal energy requirements.

Residual digestate would contain a recoverable solid fiber that would be treated to produce a farming soil improver. After fiber removal, the liquid filtrate could be spread directly onto farmland for its nutrient value, with has combined nitrogen, potassium, and phosphate (N-P-K) percentages ranging from 3-4.5 percent on a dry matter basis. If warranted, these biofertilizers could also have been enriched with minerals and microorganisms customized to mitigate depleted soil. Surface application of the biochemical fertilizer from the PRIME complex would also allow the use of lower input farming practices, contrasted with more energy intensive plowing practices. This would significantly reduce fossil fuel use, augment carbon sequestration, and help prevent soil erosion.

Sugarcane and Starch Processing Wastes in Brazil and Asia

Most of the discussion above has focused on the model of biodigestion integrated with grain-based or biomass-based ethanol production in North America or Europe, with opportunities to codigest wastes relevant to those economies. Brazil and also India, whose large-scale fuel ethanol production models are sugarcane-based, present a different picture.

- Brazil

Most mills co-produce some sugar seasonally, along with ethanol, while at other times one or the other may be the sole product. The mills also generate large quantities of gaseous CO_2, liquid residues (vinasse) and solid cane residue lignocellulosic biomass by-product (bagasse), which currently have very little or even negative value. By using steam turbines fueled by bagasse combustion in simple and often inefficient boilers, electric power is typically generated at a rate of about 1.0 MWh per m^3 (264 gallons – 3.8 kWh per gallon) of ethanol produced.

Anaerobic digestion can be applied to vinasse to produce enough biogas for an additional 0.5 MWh per m^3 of ethanol, bringing total electric power production from by-products to 1.5 MWh per m^3 of ethanol (5.7 kWh per gallon). Such operations are currently implemented at some distilleries at full scale.

It has been shown at bench scale that applying anaerobic digestion to bagasse and burning the non-biodigestible residual can increase power output to 2.25 MWh per m^3 of ethanol (8.5 kWh per gallon), but the economic feasibility of this option depends on the maximum loading rate of the bagasse biodigester and the energy price. At the current ethanol production level of over 15 million m^3 per year, the power generation potential is over 2.5 GW, which represents about 5 percent of the power demand in Brazil.

The digested wastewater contains about 70 percent of the nutrient demand of the cane fields, which can be recycled. A preliminary economic evaluation shows that productive use of the by-products of ethanol distilleries is economically feasible if the power price is more than US$30 per MWh, which is under the current typical power price in Brazil. Another important advantage of the rational use of by-products is that the generation of electric power has the potential to reduce the emission of CO_2 by 0.8–1.2 ton per m^3 of ethanol compared to generation using natural gas.

- India

A biomethanation system offered by Praj, one of India's leading biofuels facility designers, uses a mixed tank biodigester, called Ecomet XT, to convert organic wastes, including sugarcane ethanol plant vinasse into biogas. The biological conversion process occurs at mesophilic temperature in a controlled atmosphere, aimed at maximum conversion efficiency and production of biogas. The Ecomet XT system is designed to handle multiple challenges: the highly toxic vinasse, with its suspended solids, toxic compounds, and high COD; BOD in wash streams; load shocks arising out of the nature of the distillery operations and variations in feed characteristics; and variations in temperature conditions. Key features of Ecomet XT claimed by Praj are:

   - Reactor geometry and unique design of the mixing system to ensure efficient mixing of organic matter with suspended biomass to optimize reaction time
   - A hydraulic retention time designed to handle high COD loading without dilution, thereby reducing water consumption, and thus cost of treatment. This also avoids shock loading and malfunctioning of the reactor
   - A parallel plate clarifier system for separation and recycle of biomass to the reactor to maintain optimum biomass levels, ensuring a high level of biogas generation

- Design of the sludge receiving and settling system to prevent buildup of inorganic solids in the reactor, which allows consistent performance over a longer period
- Minimum reactor internals to prevent buildup of inorganic sludge, and ensure maximum utilization of reactor volume over a longer period
- A heating and cooling system designed to help ensure consistent performance in colder weather

Praj recommends that sugar-based fuel ethanol plants can integrate vinasse biodigestion with multi-stage evaporation of the vinasse feed, composting of biosolids (sludge) from the digestion along with other biosolids generated in the process, including bagasse fines.

- Thailand

A waste-to-energy project, located near Korat, Thailand, produces methane from cassava (tapioca) starch processing wastes. It is implemented by a leading company in Thailand’s key agricultural sector, Sanguan Wongse Industries (SWI). The project could serve as a model applicable to similar operations to produce methane in tropical and subtropical climates from high-starch effluents from food processing as well as biofuels plants handling feeds such as tapioca, rice, and potatoes. Its motivation is both to reduce fugitive greenhouse gas emissions of biomethane, and to reduce the use of fossil fuels for energy generation.

The project is summarized as follows:

- The Korat Waste to Energy Company (KWTE) is implementing an Anaerobic Baffled Reactor (ABR) at the largest starch production facility in Thailand
- The ABR utilizes organic material formerly emitted in wastewater to a series of ponds that were failing to aerobically reduce the organic material released, and a number of earlier ponds that were anaerobic in nature, producing vast amounts of biogas methane as a fugitive greenhouse gas
- Biogas produced is used in the SWI facility to dry the wet starch cake to the final dry starch product, a process which otherwise would use fuel oil. Nearly 8 million liters of fuel oil are displaced with renewable biogas. Excess methane is used in electrical generators to displace grid-supplied electricity. A unit with 3.0 MW generation capacity is to be installed, with another 1.0 MW to potentially be added later. Initially, surplus biogas, where produced, is flared rather than released to the atmosphere. Where possible, additional generator sets may be added, with excess generation exported to the grid. This project is the first of a series planned for this site, as the facility expands its production of modified starch. Current plans at SWI are to build a large, new facility on the same site to cope with increased demand for modified starch, with the current facility continuing to produce native starch

Model for Advanced Anaerobic Digestion in Lignocellulosic Fermentation

The anaerobic wastewater treatment modeled for converting the residuals of switchgrass fermentation is based on a series of studies sponsored by NREL and culminating in the latest work, partly derived from an 8-year effort, under Dr. Lee Lynn of Dartmouth College, et al, "The Role of Biomass in America's Future". It uses attached film anaerobic digestion, which enables conversion of high chemical oxygen demand (COD) streams, reduces treatment chemicals requirements, and eliminates the need for agitation energy. This is integrated with drying of the solid residue with full latent heat recovery of evaporated water. The anaerobic digestion is followed by an aerobic residual stabilization step. The system is projected to yield 80 percent recovery of the energy in the residuals, versus 30 percent in previously considered approaches of concentration and combustion of the residual syrup itself, according to the Lynn report. The attached film anaerobic digester design model is different from and represents an improvement on the previous NREL work, which used a suspended sludge design. It is claimed that this enables 98 percent COD conversion versus 90 percent for NREL's design, and eliminates the need for power-intensive agitation.

Typical parameters for this treatment, from the Lee Lynn (Dartmouth) study, are listed in Table 3.10.

Table 3.10 Wastewater Treatment Model – Typical Design Parameters

Parameter	Value
Inlet COD to anaerobic digester	27 g/L
Inlet BOD to anaerobic digester (70 percent of COD)	19 g/L
Anaerobic digester temperature	35°C
COD conversion efficiency	98 percent
CH_4 produced	8,677 kg/hr
Effluent COD from anaerobic digestion	500 mg/L
Aerobic treatment temperature	25°C
Aerobic COD conversion efficiency	90 percent
Effluent COD from aerobic treatment	85 mg/L

The feed to this unit is on the order of 500 million Btu per hour of lower heating value. For a system of this scale, estimated installed equipment costs are about $19.5 million, and estimated total installed capex is about $40 million.

3.2.6.2 Landfill Gas

Solid Waste Fundamentals

Solid waste found in various landfills around the world is comprised of several categories and subcategories, each with distinctive characteristics:

- Municipal solid waste (MSW), including most non-hazardous industrial and commercial wastes, classified as:
  - Organic (combustible) fraction
  - Putrescible – food waste (from wholesale and retail handling, industrial, commercial or home preparation, and post-meal discards), yard waste (grass

  - clippings, leaves, plants trimmings, etc.), animal carcasses, personal sanitary articles (disposable diapers, etc.), etc.
  - Non-putrescible – paper, wood, fabrics, plastics, rubber, wax, solvents, oils, etc. (note, each of these has some potential for aerobic and/or anaerobic biodegradation, but at very low rates)
  - Inorganic fraction– metals, glass, ceramics, stone, ashes
- Sewage treatment sludge
- Hazardous industrial waste:
  - Toxic, corrosive, flammable, reactive, or radioactive
  - Bio-hazardous (including hospital "red bag" wastes)
  - Asbestos
  - Industrial sludge (biopond waste treatment or other, process sludge)
- "Special" wastes, including:
  - Spent batteries
  - Fluorescent and other special lighting containing heavy metals
  - Out-of-date pharmaceuticals
  - Computers, cell phones and other electronics wastes
  - Rubber tires, and automobile demolition "fluff" (non-metals, excluding, liquids etc., mostly plastics and mixed materials),
  - Industrial filters, painting and coating wastes

Sewage treatment sludge is often "landfarmed", or spread out on forest, grassland, or farmland, as a soil amendment, or composted, usually in combination with other organic materials, but it is also sometimes put in landfills. This type of sludge, even when mechanically dewatered to the practical limit, contains a high percentage of water (60-90 percent), and so, through its moisture contribution, can affect the rate of conversion of other MSW co-disposed in the landfill, leading to greater landfill gas (LFG) generation rates.

Hazardous wastes are usually disposed of in separate landfills. In the US and in a number of other economies, there are several discouragements for the disposal of hazardous wastes, except as a last resort to incineration, neutralization, and other relevant types of treatment. These types of waste are generally not biodegradable, and the types of landfills used for them are more tightly sealed against water infiltration and leachate production.

The primary wastes resulting in methane generation ("methanogenisis') in landfills, therefore, are the putrescible fraction, and under certain conditions, paper. All other non-putrescible organic waste components are minor factors in LFG generation. Inorganics do not contribute LFG methane content. Food preparation practices, culture, climate, and the limited levels of prosperity in many emerging economies result in MSW steams that are higher in organic fraction, and particularly, food preparation wastes, than in more developed economies. Organic fractions can be as high as 85-90 percent in some of the less advanced economies, with limited use of disposable packaging, and daily food preparation by hand from raw ingredients at home. Much packaging is limited to paper and plastic films and fabrics, and some glass and plastic bottles and metal cans. The latter types of packages are largely either recycled, reused, informally scavenged from the MSW, or can be readily hand-picked using cheap labor in a materials recovery facility (MRF) associated with landfilling, composting, or combustion (waste-to-energy or WTE).

A major problem with many landfills (or “dumps”) in emerging economies is typically their informal, haphazard design, without proper impervious linings for leachate (garbage juice) collection, daily capping with earth of isolated “cells” of the waste materials, compaction, or venting to prevent LFG migration and to collect LFG for flaring or use. Scavengers often frequent these open dumps and create hazards for themselves by exposing themselves to toxic, contagious, or otherwise hazardous materials, and often to others by setting fires to recover metals or by spreading disease. Many of the emerging economies, especially in North and South Asia, Southeast Asia, Africa, and Latin America, are working towards improving these conditions and installing quality landfills.

The generation of MSW varies greatly among regions national economies, regions, and localities, as does the percentages and the types of waste stream fractions that are disposed treated in other ways besides in landfills.

As a point of reference, Shanghai, the largest city in China, has about 15 million people, and generates approximately 5 million tons a year of municipal garbage (far more if industrial waste is included). Shanghai, in contrast to New York, has a vast, long-standing recycling/materials reclaiming industry and infrastructure, with hundreds of centers and facilities and thousands of workers. A large fraction of the waste (over 30 percent) is recycled, but only some of the disposed material is put into covered landfills, the rest being put into open dumps at one extreme, or treated in WTE at the other extreme. The city administration has set goals for a high level of treatment or covered landfill disposal.

As another point of reference, New York City generates about 9.5 million tons per year of MSW (“garbage”), (not including construction demolition debris or industrial waste), some of which is collected by the municipal Department of Sanitation, and the rest by private carters. Subsequent to the recent closure of the Fresh Kills Landfill on Staten Island in New York City to additional disposal, all of New York City’s garbage from both municipal and private collection is shipped out of the city by barge, truck and rail to landfills in other parts of the economy, at a cost of about US$100 per metric ton.

New York had in the last few years ceased its curbside pickup of glass, plastic and metal containers, and paper for recycling, but has more recently reinstated recycling. In contrast, not only has a high percentage of packaging waste in the United States, Europe, and Japan been recycled for over a decade, but a large percentage of the remainder has been combusted in WTE facilities to generate electricity and for district heating. Tipping fees for WTE in Europe vary from US$30 per ton in Sweden to US$130 per ton in Switzerland and Germany (Waste-to-Energy Trends in Europe, Wastes Management, January 1999, Pgs. 35-36, published by Juniper Consultancy Services).

In general, because of high water content, the putrescible (solid waste that contains organic matter) fraction of MSW is a liability in WTE. In an ideal, integrated waste disposal strategy:

- Ozone depleting and GHG refrigerants, lubricating and transformer oils and solvents would be recovered and recycled by special means (e.g., drained from appliances, vehicles, equipment, tanks and containers)
- Good quality paper and textiles would be recycled for papermaking
- Certain plastics (such PET and HDPE), aluminum and steel would be recovered for materials recycling
- Some glass bottles might be scavenged or otherwise returned for cleaning and reuse
- Other glass could be separated color (usually at a central facility, such as bottling plant or distributor to which they are returned in a deposit rebate program), or crushed as mixed color cullet for glass making or used a roadbed abrasive/filler
- Miscellaneous paper, plastics and other non-putrescible organics would be separated for WTE
- Putrescible wastes would be separated for:
  - Composting, anaerobic or aerobic digestion, or
  - Disposed of, along with any remainders from the above, including large items such as appliances, in landfills well-designed for LFG collection and use.

In such an ideal strategy, the emissions of LFG methane would be minimized, as would the cost of building, maintaining, and closing the landfill, if used. In Europe, an EC Directive requires composting of putrescible household and yard waste.

LFG Methane Generation

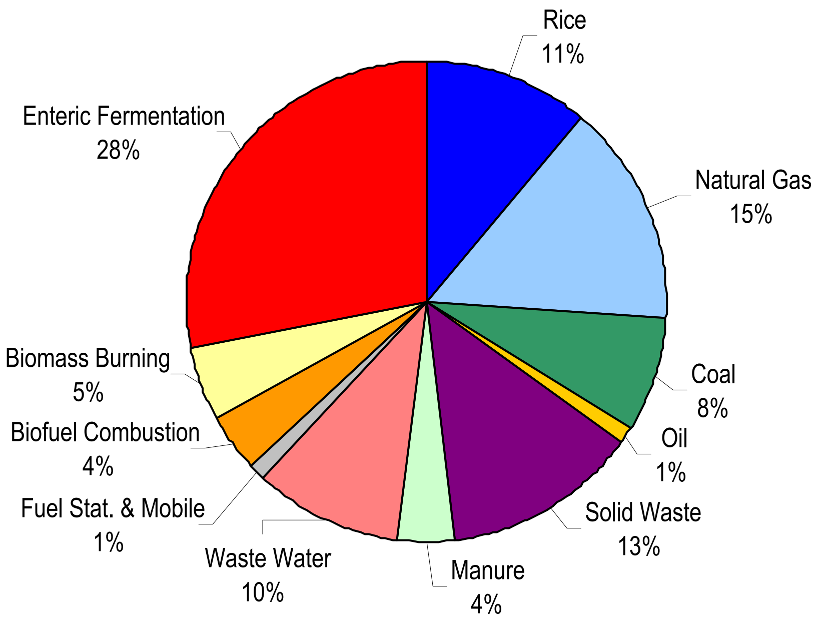
While the locations of other sources of recoverable fugitive methane - oil and gas production and midstream handling, coal mining, agricultural biomass generation, and livestock operations – bear little or no necessary relationships to population centers, which usually comprise the primary market outlets for recovered methane, landfills and sewage treatment facilities are generally in or near populated areas. As can be seen from the chart in Figure 3.27, solid waste is one of the largest sources among those that are practically recoverable for use and/or for control of greenhouse gas (GHG) emissions by flaring. That is, though livestock and other enteric generation is estimated to be somewhat larger, control of these emissions is relatively impractical, and is not feasible to bring the methane generated this way to the market. Since coal mine and coal bed sources may not be logistically suited to bring to market, it would appear that LFG is the leading contender for practical recovery with a close relationship to population, and therefore, this resource should be prioritized for consideration and development.

Methanogenesis, or methane generation in landfills, is a result of anaerobic decomposition of organic materials. Major factors affecting emission rates are:

- Amount and “quality” of organic material deposited in landfills
- Rate and distribution of anaerobic decomposition in different zones of the landfill
- Moisture and oxygen levels (which may be controlled in “bioreactor” type landfills)

- Landfill design and construction
- Landfill methane collection and combustion, if any (e.g., energy use or flaring)

Figure 3.27 Global Anthropogenic Sources of Methane by Source



Organic material deep within landfills takes many years to completely decompose. Therefore, past landfill disposal practices greatly influence present day emissions.

There are many other factors that influence the rates of methanogenesis – factors that vary as a function of societies and cultures. For example, as suggested above, in developed and industrialized economies the waste stream tends to be drier and contains many materials that are often recovered or informally scavenged before disposal from landfills in developing economies, (e.g., plastics, paper, wood, rags, etc.) Further, if landfills (rather than central or random, roadside dumps) are used at all in developing economies, per capita rates of waste generation tend to be much less. The putrescible solids (primarily wet vegetable wastes) content is much higher, they are rarely built to expensive design specifications as are landfills in developed economies, and they are often not lined, resulting in a drawing off of moisture in the form of leachate. Loss of leachate may also result in drier conditions, which slows the rate of methanogenesis, since the rate of methanogenesis is in part moisture-dependent, as previously stated.

Methanogenesis of carbohydrates, including sugars and cellulose, produces a mixture of approximately 50 percent methane and 50 percent carbon dioxide (CO2), rendering LFG a low-to-medium heating value gas. LFG also contains a small percentage of water and non-methane organic compounds (NMOCs). Sulfur and nitrogen, found in food wastes and other putrescible solids may also lead to contamination of the gas with hydrogen sulfide, other odorous sulfur compounds, ammonia, etc., which require removal for most applications.

Options for the disposition of LFG are:

- Flaring
- Industrial use as low-to-medium Btu power/heat fuel gas with the worst impurities removed and piped short distances
- District heating
- On-site power generation
- Removal of CO_2 and other impurities and addition to a distribution pipeline
- Heating and lighting of greenhouses near the site

LFG Recovery

A landfill gas system is used to collect and control gas emissions through a system of wells and it also prevents subsurface migration of gas off site. If not controlled, gas can build up pressure to an explosive level and/or cause harmful air pollutants as well as GHG methane to be emitted into the atmosphere.

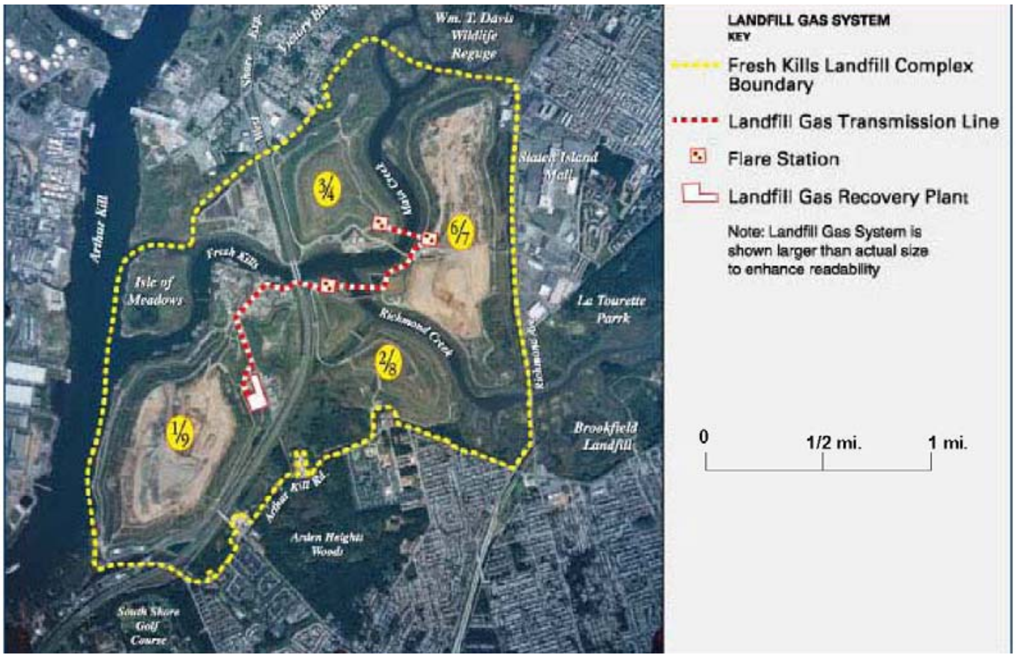
In the meantime, the Fresh Kills Landfill has become a major generator of LFG, and has an advanced LFG recovery system installed. This landfill is one of the largest manmade structures in the world and is discernable from earth orbit. Figure 3.28 shows an aerial view of Fresh Kills Landfill with the LFG collection, flare, and utilization system shown in schematic.

The New York Department of Sanitation (DOS) has been recovering gas and processing it from a portion of Section 1/9 since 1982. Currently, a system of flares operates to burn off the portion of the gas that is not recovered from sections 3/4, 2/8 and 6/7. The LFG recovery plant and related systems, when complete, are estimated to be able to provide enough fuel for the cooking and heating needs of close to 25 thousand homes.

Typically, a large number of vertically driven gas wells (10-200) are constructed on a landfill to extract the landfill gas as it is produced. Gas is drawn from the wells through pipework to treating equipment, which removes moisture and harmful components such as sulfur compounds, ammonia, traces of halogenated solvents, etc. After appropriate cleaning and treating, the gas can be used, for example, for electricity generation in either a reciprocating internal combustion gas engine or a microturbine, with any surplus gas being flared.

An active recovery system collects the LFG from the extraction wells under vacuum pressure. This system moves the gas through a network of pipes. The pipes increase in size as they move toward the perimeter of the landfill, reaching flare stations or the gas recovery plant.

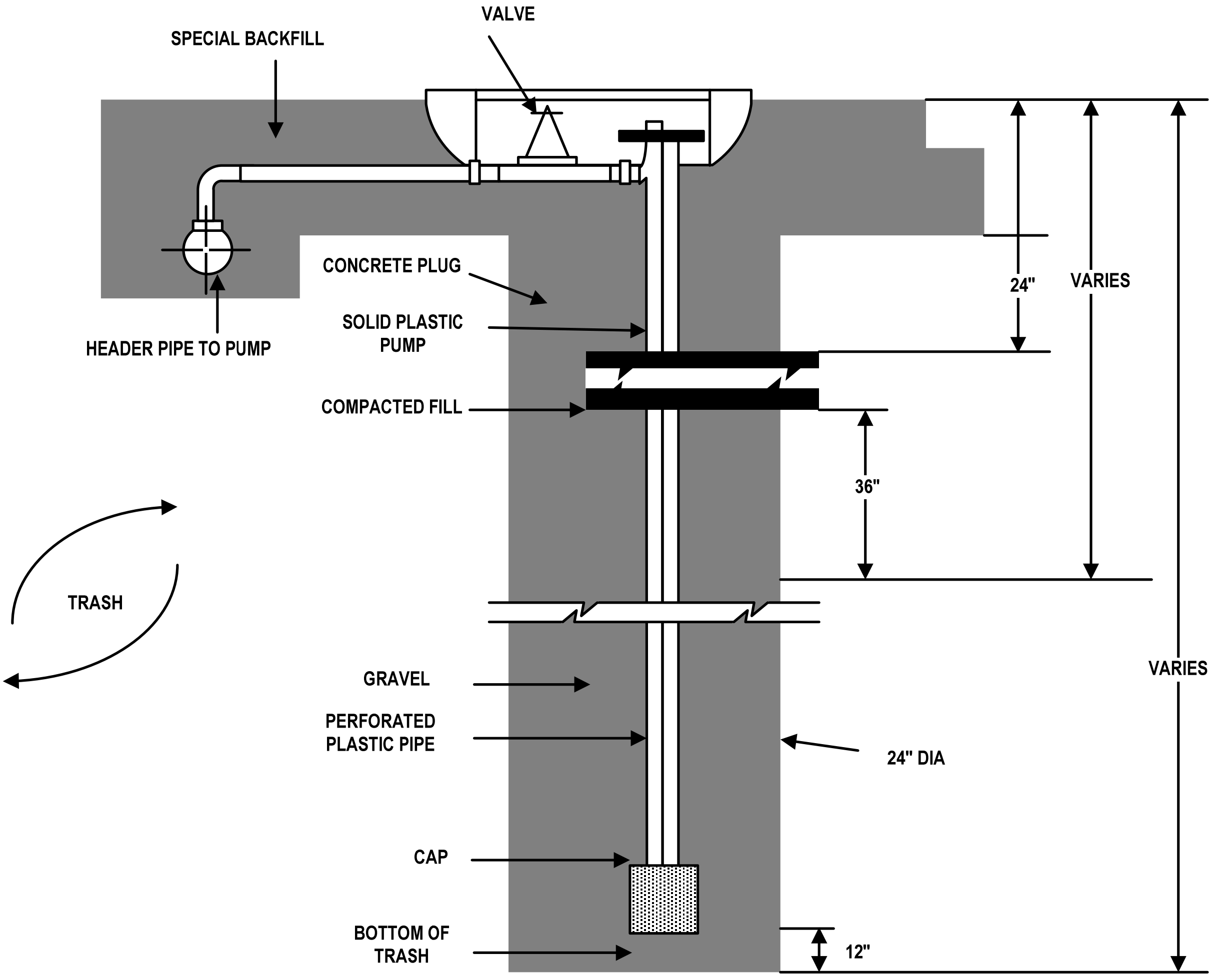
Figure 3.28 Aerial View of Fresh Kills Landfill, New York City



Source: New York Department of Sanitation

A typical collection system, such as Fresh Kills, consists of LFG extraction wells placed at approximately every acre. A pipe extends down through the depth of the refuse or to groundwater table, if higher. Beyond roughly the first 20 feet below the surface, the well pipe is perforated. The well and the geomembrane are sealed with synthetic rubber and stainless steel fixtures. Above the topsoil, the well is typically attached to flexible tubing connecting to a network of lateral header pipes, lying on top of the geomembrane or clay lining. Water in the LFG condenses, is collected in tanks, and is pumped out. Figure 3.29 is a schematic of a typical LFG extraction well, taken from a USEPA report, *"Turning a Liability into an Asset: A Landfill Gas-to-Energy Project Development Workbook"*, EPA 430-B-96-0004, Sept. 1996, pg. 3-2.

Figure 3.29 Typical LFG Extraction Well



Via the lateral pipes, the gas moves to the gas recovery plant or to flares. If used, flares, usually combust the LFG at temperatures between 1,600-2,000°F. Methane, NMOCs, hazardous air pollutants, emissions, and odors are reduced by almost 100 percent. When LFG is recovered for use, flares serve as a safety back-up measure in the event the recovery system is down. As the LFG production winds down, when little or no gas is generated, and the active extraction system is no longer productive, the remaining methane can either be flared or vented passively into the atmosphere through the previously fitted.

Other Elements of a Managed Landfill

- LFG Migration Control

Independent of the active gas extraction network, as a safety measure to ensure that no gas migrates off site, a passive venting system is sometimes placed around the perimeter of the landfill. Passive vents keyed to low permeable soils or below the seasonal low groundwater table form an effective barrier to stop the movement of gas off-site. Such a system often appears on the surface as a channel of coarse stones mounded up around the perimeter. Additionally, subsurface cut-off walls for the leachate can be placed to further prevent migration of gas off-site. Monitors are often placed outside the trench to ensure that gas has not migrated off-site. In addition, utility trenches should be sealed to eliminate potential off-site routes for LFG.

- Leachate System

Leachate is created as water comes in contact with garbage. The goal of the leachate management system is to contain, collect, and treat leachate before it reaches adjacent surface waters and groundwater, or damages the topmost landfill cover. This is achieved both by minimizing the amount of water that comes in contact with refuse and treating the leachate that is created. As the final cover is placed on the landfill, the production of leachate will diminish; however, water remaining in the landfill will cause the continued production of leachate. Storm water management systems are also designed to prevent the production of leachate by removing water as quickly as possible from the landfill face.

An integral part of the leachate control system is often silt or clay layers beneath the landfill that form a relatively impermeable barrier between refuse and the groundwater table below. The leachate that gravitates through the refuse mass downward and outward to the perimeter is collected before it can escape from the landfill. Perimeter collection drains are located outside the footprint of each section. The drains are placed below groundwater level (typically from 5-50 feet below the surface). This positioning of the drains establishes higher pressure on the outside of the drain so water and any escaped leachate is pushed inward toward the landfill. The drains are connected to trenches that are connected to collection wells and pumps.

Leachate is pumped from the collection pumping wells to a pump station and conveyed to a leachate treatment plant. The leachate is treated to remove pollutants before being discharged, and is monitored to ensure that effluent levels are acceptable. The plant can have a large treatment capacity (e.g., Fresh Kills capacity of 1 million gallons per day).

- Cost Factors

The detailed cost information below is based largely on a USEPA report, “Turning a Liability into an Asset: A Landfill Gas-to-Energy Project Development Workbook”, EPA 430-B-96-0004, Sept. ’96, chapters 3.0 and 5.0, with capital and operating costs escalated to a 2004 current US$ basis (2004/1994 O&M=1.36; 2004/1994 CAPEX=2.28).

LFG Collection and Cleaning

Total LFG collection system costs can vary widely, as a function of a number of site-specific factors. If the landfill is deep, collection costs will tend to be higher because well depths and volumes of LFG generated per well are greater. Collection costs also increase with the number of wells installed. Table 3.11 presents estimated capital and operating and maintenance costs for collection systems (including flares) at typical landfills with 1, 5, and 10 million metric tons of waste contained. As a point of reference, New York City would fill the largest of these typical landfills with one year’s collections – currently about 9.5 million tons per year.

Table 3.11 Typical LFG Collection Costs and Energy Available

Landfilled MSW in place, million metric tons	1	5	10
Estimated gas generation (mcf/day)	642	2,988	5,266
Collection System Capital cost (US$000)	804	2,673	4,607
Collection System Annual O&M (US$000)	121	207	296
LFG Output (million Btu/year)*	100,000	490,000	850,000

* Assumes a 90 percent availability factor

Assuming a heat rate of 11.4 million Btu/MWh for power generation with LFG (in a typical small Internal Combustion Engine, or ICE), the typical landfills considered of 1.0, 5.0, and 10.0 million metric tons of MSW in place could generate 7.8 GWh/yr (989 kW), 38.2 GWh/yr (4,845 kW), and 66.2 GWh/yr (8,397 kW), respectively.

Flaring costs are incorporated into the estimated costs of LFG collection systems because excess gas may need to be flared at any time, even if an energy recovery system is installed. Flare systems typically account for 5 to 15 percent of the capital cost of the entire collection system (e.g., including flares). However, flare costs will vary with local air pollution control monitoring requirements and the owner's own safety requirements. For example, if the flare is enclosed in a building for security or climate reasons, the proceeding cost figures would increase by approximately $166 thousand [Nardelli, 1993, escalated to 2004 basis]. Annual operation and maintenance costs for flare systems are typically less than 10 percent of the total collection system costs, and thus range from approximately $10,900 for a 1 million metric ton landfill, increasing to $20,400 for a 5 million metric ton landfill and $28,600 for a 10 million metric ton landfill.

After the landfill gas has been collected, and before it can be used, it must be treated to remove any condensate that is not captured in the knockout tanks, as well as particulates and other impurities. Treatment requirements and costs depend on the end use application. Minimal treatment is required for direct use of gas in boilers, while extensive treatment is necessary to remove CO_2 for injection into a natural gas pipeline or for conversion to vehicle fuel. Power production typically involves cleaning in a series of filters to remove impurities that could damage engine components and reduce system efficiency. The cost to filter the gas and remove condensate for power production is considerably less than the cost to remove carbon dioxide and other constituents for injection into a natural gas pipeline or for compressed natural gas (CNG) or liquefied natural gas (LNG) use in vehicles.

On-site Power Generation

The following Table 3.12 presents a sample on-site power generation project (which would relate to a landfill, on the basis presented above, of about 10.0 million metric tons contained). The LFG collection system costs are approximately as assumed above and the power generation is assumed to be in a packaged system costing less than US$1,000 per kW installed. This project is assumed to have an effective annual capital burden of about 18.4 percent on capital investment, calculated as an 8-year loan made to the project with a 10 percent interest rate. If the project were financed on the basis of a typical industrial project, with an expected 20 percent return on investment (ROI), and including 20 percent depreciation (more typical of private, short-term investment scenarios in high-risk situations), the cost of the electricity would be approximately US$0.0422 per kWh. Such a project might be financially attractive, depending on local conditions such as power costs, grid reliability, etc.

Table 3.12 Economics of a Hypothetical LFG-to-Energy Project

Cost items	
Annual generation (GWh)	67.8 GWh
Estimated total cost of project (million US$)	12.2
Annual debt service payment (8-year loan, 10 percent interest) on a per kWh basis (US$/kWh)	0.0326
Operations & Maintenance – O&M (US$/kWh)	0.008
Administration & Insurance (US$/kWh)	0.0016
Total generation cost (US$/kWh)	0.0422

Source: The Prototype Carbon Fund -Durban, South Africa
Landfill Gas to Electricity -Project Design Document, July 2004 Report

Upgrading LFG to Pipeline Gas Quality

The most common set of market options for LFG are on-site power generation to supply on-site power needs (leachate handling, lighting, etc.) as well as for power export to the grid, and short distance transmission of low-medium heating value gas to adjacent industrial users. However, it is possible to remove most or all of the contaminants in raw LFG, including CO_2, to produce a high methane concentration for blending with pipeline gas for longer distance transmission to market. Upgrading LFG to pipeline gas quality is relatively expensive, because of substantial processing requirements to remove CO_2, nitrogen and other constituents of raw landfill gas. This option is currently viable for larger landfills (e.g., more than 4 million cubic feet per day, or, typically, with 8-10 million metric tons of MSW contained). At such capacities, significant economies of scale are possible. It is estimated (based on the USEPA LFG report cited herein, pg. 5-26) that gas prices required to support such a project would be in the range today of US$4.50 to $5.60 per MM Btu (2004$). Tax credits may be needed to assist qualifying projects to show attractive enough economics for private investors in this type of project.

Landfill owner/operators owning vehicles, garbage collection fleet operators or other nearby fleets (e.g., municipal vehicles, delivery trucks) can achieve fuel cost savings and major environmental benefits by converting these fleets to run on CNG, LNG, or LCNG (LNG used to make CNG by pumping and vaporization, rather than by compression during refueling). LNG can be made for storage and to save on CNG compression system power and capital costs. Key factors in the economic evaluation of this option are:

- Costs of installing a fueling station for either:
  - CNG - compressors and ballast pressure tanks
  - LNG - cryogenic storage and pumps, or
  - LCNG - small scale liquefaction (or SSL), plus cryogenic storage and pumps and vaporizers
- Costs of making and storing LNG for LNG or LCNG - cleaning the gas for the cryogenic cycle, plus small scale liquefaction (or SSL)
- Costs of retrofitting vehicles to run on the alternate fuel – including either a larger number of heavier CNG pressure tanks or smaller, more expensive cryogenic LNG tanks

LFG has a logical and convenient relationship to garbage truck refueling, since they frequent the landfill. Issues addressed with an LNG based system and the reasons LNG has been preferred over CNG by fleet operators and is attractive compared to diesel are:

- The energy cost of the fuel is “free”
- CNG tanks are more difficult than LNG tanks to mount on a garbage truck, with a limited body geometry
- LFG is generated continuously, but garbage trucks have limited weekly schedules, so LNG is a demand leveling strategy

The cost of installing a compressed landfill gas fueling facility can be significant - the installation of the Puente Hills Landfill fueling station in California cost approximately $1 million in 1994. Vehicle conversion costs, which currently run well over $5,000 for trucks, can also be offset by tax deductions and other government supports, as they usually are in the USA because of the environmental benefits from using natural gas alternative fuel.

Fleet vehicles are an especially good application for alternate fuels because these vehicles usually travel less than 200 miles per day and they return to a central location at night for refueling and storage. Also, having a fleet of vehicles will increase fuel usage and therefore decrease average fuel costs since capital recovery of fueling station construction costs represents the majority of fuel production costs (operation and maintenance costs for alternate fuel vehicle stations are minimal).

The technology for small-scale liquefaction useful for converting cleaned LFG to LNG is available from a number of sources; either developed for this purpose or adapted from gas distribution system LNG “peak saving” system designs:

- Black & Veatch Pritchard Inc. (BVPI) (USA and International)
- NexGen Fuelling/Chart Industries, Inc. (USA and International)

- Kryopak Inc. (USA and International)
- CNG SERVICES International, Inc. (USA and International)
- CryoFuel Systems, Inc. (USA and International)
- Applied LNG Technologies/Jack B. Kelley Group (USA)

There are also emerging (prototype and demonstration) SSL systems coming on the market:

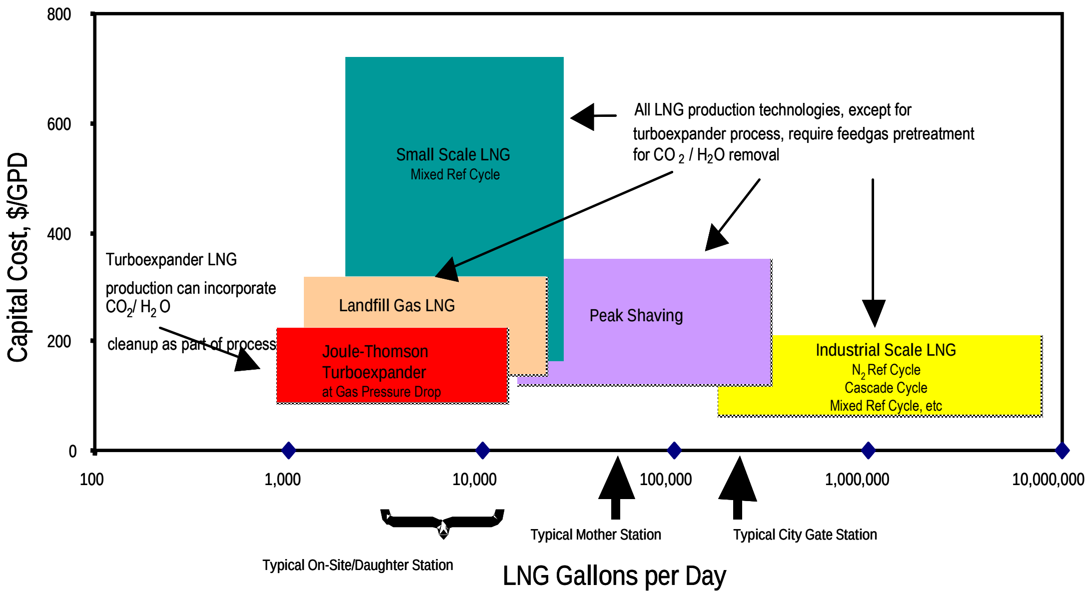
- Idaho National Engineering and Environmental Laboratory (INEEL) (USDOE) – based on turbo-expanders - versions of this system can work directly on raw LFG and remove the impurities mechanically as an icy "slush" from the LNG
- Gas Technology Institute (GTI) (USDOE)

The developing market for natural gas vehicles provides an opportunity for LNG and LNG-CNG fuelling systems that lower fuel cost at the station. Other markets for smaller-scale LNG liquefiers include flare gas from stranded gas and oil wells, coalmine and coal bed methane, and the other M2M targets discussed in this report.

SSL is fundamentally demonstrated technology. Over 55 small to medium–sized "peak-shaver" LNG plants were built in the United States over 40 years. These were mostly plants built by gas utilities to gradually build up inventories of LNG in a cryogenic storage tanks during slack demand periods for re-vaporization during periods of peak demand or pipeline problems.

Typical costs of liquefaction facilities of various sizes of interest are sown in Figure 3.30.

Figure 3.30 Typical Ranges of Capital Costs for LNG Production



Typical refueling systems costs for various types of fleets utilizing LNG are shown below in Figure 3.31.

Figure 3.31 Costs and Other Factors for LNG Fleets

Fleet Type	Transit Bus Fleet		Refuse Hauler Fleet		Other Return to Base	
Fleet Size	50	200	25	100	25	100
LNG gals*	10,000	38,000	6,000	23,000	5,000	21,000
Station Cost	$520K	$1,609K	$377K	$1,073K	355K	$948K
O&M, $/yr	$19.8K	$44.9K	$16.6K	$31.7K	$16K	$29.7K
Maintenance	$0.45/mi		$0.528/mi		$0.48/mi	

*Storage is for 3 days of operation

Add $70K for garage modifications (ventilation, CH_4 detection) if vehicles are indoors
Source : Ad Little

3.2.7 Biobutanol by Fermentation

3.2.7.1 Historical ABE Fermentation

Acetone-butanol-ethanol (ABE) anaerobic fermentation using the spore-forming bacterium, *Clostridium acetobutylicum* ("*C. acetobutylicum*" – see Figure 3.32) is one of the oldest known industrial fermentations, once second only in production volume to ethanol fermentation by yeast. However, ABE fermentation is complicated and difficult to control. It has declined and nearly disappeared since the 1950s, in favor of petrochemical routes.

In a typical ABE fermentation, butyric, propionic, lactic and acetic acids are first produced by *C. acetobutylicum*, and with the increased presence of these acids, the culture pH drops and undergoes a metabolic "butterfly" shift, after which butanol, acetone, isopropanol and ethanol are formed. Limited by severe product inhibition, butanol yield from glucose is low, typically around 15 percent, and usually not above 25 percent. Since butanol concentrations of only 1 percent can significantly inhibit cell growth and the overall conventional ABE fermentation process, butanol concentrations are usually below 1.3 percent.

Since the 1980s, there has been much engineering effort to improve butanol production in ABE fermentation, including cell recycling and cell immobilization to increase cell density and reactor productivity, and using extractive fermentation to minimize product inhibition. Despite these and other efforts, the best results obtained for ABE fermentations are still less than 2 percent butanol concentration, 4.46 g/L/h productivity, and yield from glucose below 25 percent.

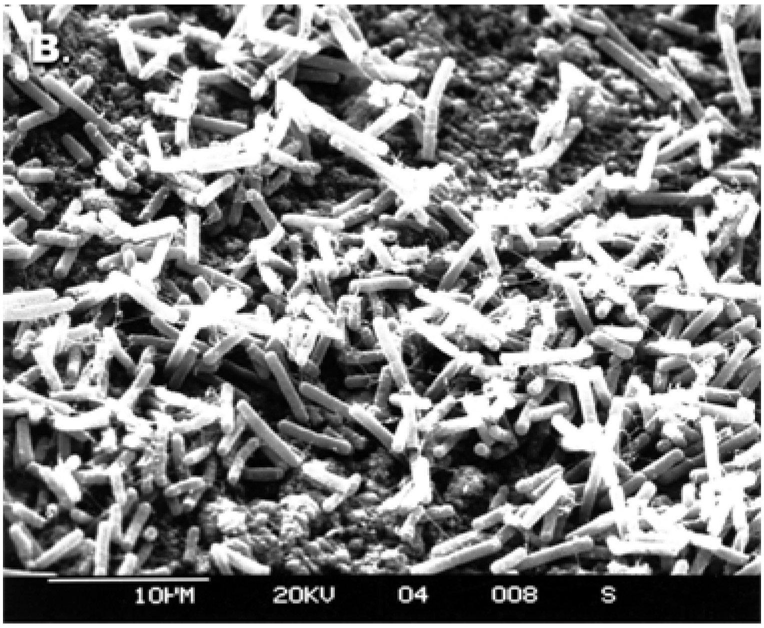
Since 2006, DuPont and BP have been in partnership to develop and commercialize biobutanol. They have commissioned a full environmental lifecycle analysis of the biobutanol production process. Initial indications from their studies indicate that, on the same feedstock basis, biobutanol delivers emission reductions that are at least as good as ethanol.

3.2.7.2 *ChemSystems Process Improvement Studies for US DOE*

The initial objective of this work was to develop a methodology for analyzing the impact of technological advances as a tool to help establish priorities for R&D options in the field of bio-catalysis. As an example of a bio-catalyzed process, butanol/acetone fermentation (ABE process) was selected as the specific topic of study. A base case model characterizing the technology and economics associated with the ABE process was developed in the previous first phase of study for JPL. The project objectives were broadened in the second phase of work to provide parametric estimates of the economic and energy impacts of a variety of research advances in the hydrolysis, fermentation, and purification sections of the process. The research advances analyzed in the study were based on a comprehensive literature review, and the criteria employed in the selection process included information availability, technical feasibility, energy consumption and economics.

These advances were analyzed individually as well as in selected combinations in order to assess their overall impact relative to the base case. In addition, a hypothetical "best case", combining the best elements of each process improvement, was constructed for the overall production process.

Figure 3.32 Scanning Electron Micrograph of *C. acetobutylicum* *(2300x)*



Source: Quershi, N, et al., Appl. Microbial Biotechnology 1988, 29:323–328.

The six process options analyzed were as follows:

- Continuous ABE fermentation
- Vacuum ABE fermentation
- Baelene solvent extract ion

- HRI's Lignol process
- Improved pre-hydrolysis/dual enzyme hydrolysis
- Improved microorganism tolerance to butanol toxicity

Most experts would agree that this aspect of microorganism tolerance to butanol toxicity remains today the most salient challenge to process development.

3.2.7.3 METabolic Explorer (METEX – France)

METEX estimates the global biobutanol market at about \$3.5 billion per annum, paints, coatings and solvent applications, and aim for production costs at least 50 percent less than the petrochemical route. Their focus areas for development include biobutanol and propylene glycol, or 1,3 PDO. Nexant obtained non-confidential information from METEX, the work that METEX is doing to produce biobutanol with a genetically modified clostridium acetobutylicium bacterium, used in the ABE anaerobic fermentation route.

METEX identified some major industry needs going forward as:

- To produce a "stable" *clostridium bacterium* (The classic strain "drifts" away from the desired strain/characteristics. Their bioengineering focus is to eliminate all enzymatic pathways that detract from a focus on producing butanol)
- Increase yield of butanol by eliminating acetone pathways (which METEX claims to have done)
- Decreasing ethanol co-production (with which they claim to be far along)

METEX claims to have unique genetic "tools" to work with the *clostridium bacterium*, and that they are able to use these genetic tools to remove the undesirable pathways in order to favor the production of butanol with little ethanol, no acetone, and minimum organic acid by-products. The best mix they have so far is with a ratio of butanol:ethanol of about 9:1. Additionally, they claim that this improvement on the butanol reaction kinetics will not have any adverse effect (e.g., inhibition) on cell growth.

Butanol is much easier to remove from the fermentation medium than ethanol. The upper level of butanol in the broth is 2 percent (higher becomes toxic to the *clostridium bacterium*), and eventually might approach 3 percent. The classic technique, which they will employ, is cycle gas stripping of the butanol followed by condensation.

They confirm their work shows the *clostridium bacterium* can use a wide range of substrates – glucose solution, sugarcane juice, grain mash (starch directly), biomass-derived C_5-C_6, corn zylan, etc., but not molasses, which has too high a salt content. They point that *clostridium* produces its own cellulase enzymes that could theoretically digest crystalline cellulose, but expression of these have not been made functional yet. METEX is working on enabling this function.

METEX does not think that a pre-treatment process will have any inhibition issues if cellulosic substrates are used as the feedstock for their process, but they have no experience with AFEX or high lime pretreatments. In any case, they are aiming for a system that will metabolize cellulose without hydrolysis, though it might benefit from lignin-removing pretreatments. Patents have been filed but are not yet issued.

METEX projects that their first plant will start up in 2011, with capacity of 100 thousand tons. They have not announced where, but probably not in France. They plan to license their technology (non-exclusively). They do not expect that they will change microbes before they commercialize their first plant.

Although they will not disclose the detailed process characteristics (e.g., conversion, yield, etc.) and any preliminary economics that they have done, they say the total yield of solvents (e.g., butanol, acetone and ethanol) is better than the classic route's 0.33 grams of solvents (ABE) per gram of glucose. Yield losses are largely due to the acetic and butyric acid by-products. They claim they are at least 30 percent cheaper than the current petrochemical route to butanol.

They perceive their major competitors using different bacteria than *clostridium* (e.g., the well known, but less directed *E. coli*), such as those described in the DuPont patents, to produce butanol. They expect capital requirements among the competing technologies to be very similar. They do not foresee any "unexpected" newcomers before METEX commercializes its process in 2011, as the development of bacteria is a time-consuming process and from 2007 and 2011 is too short to develop any new bacteria of significance (it is easier to delete pathways as they have done than to add them as DuPont must).

3.2.7.4 Tetravitae/Blaschek – C. beijerinckii Based Fermentation

Hans Blaschek is participating as co-founder and Chief Science Officer in Tetravitae Bioscience Inc., with headquarters in Chicago, IL, and a technical facility in Champaign, IL. Tetravitae is commercializing the clostridium-based biobutanol technology that he, Nasib Qureshi, and others have been developing over the last decade, and particularly, their most recent process advances with the (not transgenic) *C. beijerinckii* BA101 strain, which was mutated by chemical stress from the wild strain, *C. beijerinckii* NCIMB 8052. Because the biofuels industry is faced with society's food-versus-fuel concerns, and because butanol's toxicity limits its concentration in the fermentation broth to low levels (relative, say to ethanol fermentations), the team has sought an integrated approach utilizing biomass feedstocks, by using both a better microbe and improved engineering designs. These improvements include:

- High yields of butanol versus acetone, ethanol, and acid by-products
- High levels of conversion of C_5 sugars from biomass cellulose and hemicellulose
- Continuous fermentation processing
- Solvent stripping during fermentation to increase fermentation volumetric productivity

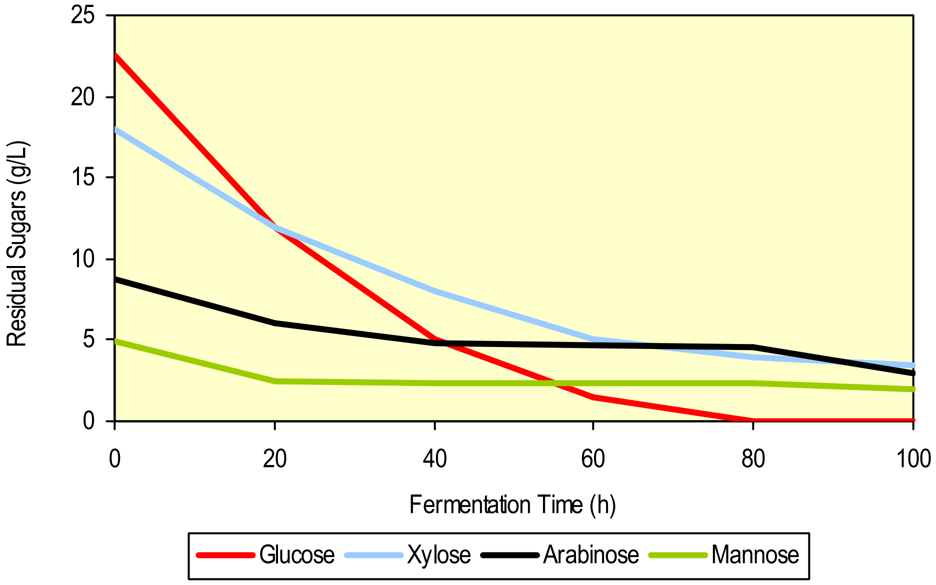
High Butanol Broth Concentrations

As mentioned above, the BA101 strain was developed in the early 1990s using chemical mutagenesis together with selective enrichment on the non-metabolizable glucose analog, 2-deoxy-glucose. The team ran pilot scale (20-liter) fermentations using 6 percent glucose or maltodextrin, which demonstrated that BA101 produces twice as much butanol as the parent strain used for mutation. In addition, it was shown that BA101 exhibits reduced acid production and increased carbohydrate utilization. *C. beijerinckii* BA101 produces over 20 g/l of butanol in 50 hours (US Patent 6,358,717), contrasted with the parent strain of *C. beijerinckii* NCIMB 8052 producing about 8 g/l in 80 hours. In terms of improved volume utilization, for butanol broth concentrations of 10 g/l, BA101 can produce 0.38 g/l-hr, while NCIMB 8052 could only produce 0.1 g/l-hr.

Pentose Utilization

The testing also established a high degree of utilization of pentoses, as indicated in Figure 3.33, from a presentation, The Acetone-Butanol-Ethanol Fermentation and the Road to Commercialization by H. Blaschek, October 16, 2007, at Platts' 2nd Annual Cellulosic Energy Conference in Chicago, IL.

Figure 3.33 BA101 C_6 and C_5 Sugar Metabolism



Inhibition of the fermentation by the byproducts of pretreatment and hydrolysis, or by tramp materials or organisms carried by the feeds, is a major concern in utilizing lignocellulosic biomass as a fermentation substrate, which is a primary goal of much biofuels development. *C. beijerinckii* strains can concurrently utilize different (hexose and pentose) sugars prepared from lignocellulosic feeds for ABE production. For example, at the concentrations tested, furfural and HMF, typically found in pretreated hydrolysate, have no inhibitory effects on *C. beijerinckii* BA101. However, other commonly found compounds, syringaldehyde, ferulic and p-coumaric acids were potent inhibitors of ABE production by *C. beijerinckii* BA101. Hot water and AFEX treated systems were tested, as were straw, DDGS, and other potentially usable cellulosic substrates.

Continuous Fermentation with Solvent Stripping

With solvent stripping, as illustrated in Figure 3.34, recycle gas (CO_2, with some H_2) is bubbled through the fermentation broth and circulated though the condenser. ABE solvents generated in fermentation are condensed in a condenser and the gas is recycled back to the reactor. The ABE mixture is recovered as a liquid solution for distillation separations. Except for the exchanger and blower, very little apparatus is required beyond the fermentation system. In contrast to continuous membrane removal of butanol during fermentation, which is proposed by some, the system is not in mechanical contact with the broth, and does not foul, nor does it remove nutrients or intermediates (e.g., acids). Its greatest usefulness to the process is in reducing butanol concentration below physiologically toxic levels. The condensate is such that it allows for recovery of concentrated AB product streams.

Table 3.13 shows the experimental results that are evidence of the high productivity potential of this technology in a continuous reaction mode with solvent stripping.

Figure 3.34 Biobutanol Fermentation with Continuous CO_2 Stripping

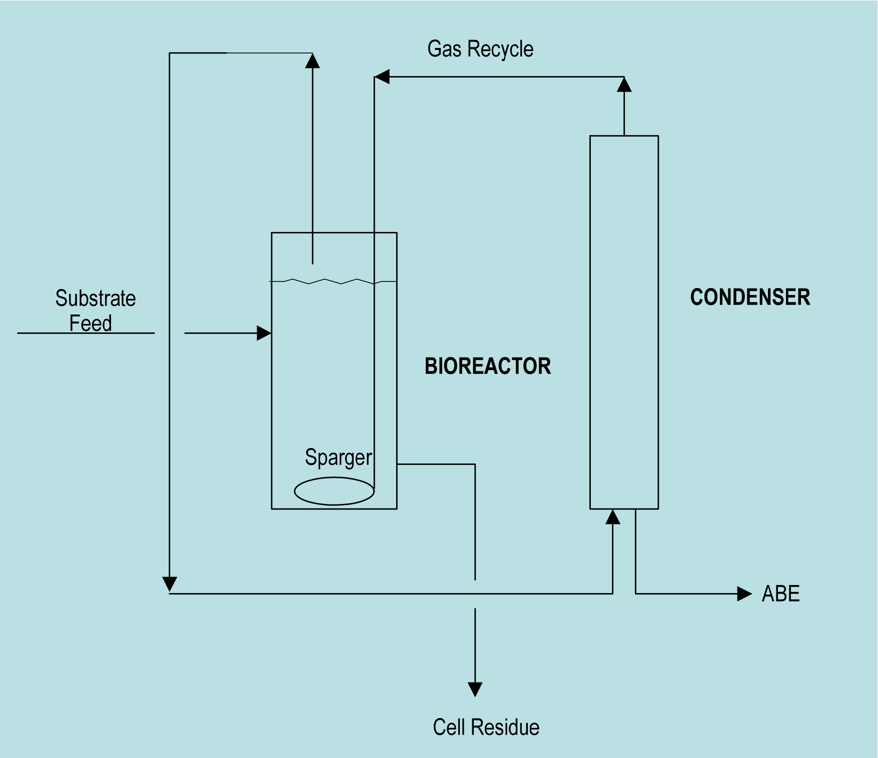


Table 3.13 Continuous Fermentation with Stripping

(Productivity Improvements)

Product	Batch	Batch w/ Stripping	Fed-Batch w/Stripping	Continuous w/ Stripping
Acetone (g/L)	5.3	6.9	77.7	204
Butanol (g/L)	11.8	16.4	151.7	251
Ethanol (g/L)	0.5	0.3	3.4	5.1
Total ABE (g/L)	17.6	23.6	232.8	460.4

Glucose utilized	75.30%	100%	100%	N/A
Productivity (gL/h)	0.29	61	1.16	0.91

In April 2006, Professor Hans Blaschek (University of Illinois) reported significant advances in fermentation butanol using his patented, genetically modified organism *Clostridium beijerinckii* to convert corn into butanol, which he has been developing since the 1990s. He reported successfully mapping and analyzing the organism's genome and the information allowed development of a second-generation strain of the microorganism that is more effective. The University of Illinois was issued a patent for the mutant strain *Clostridium beijerinckii* BA101 in 2002 (US 6,358,717). *C. beijerinckii* was chosen by the US DOE for gene mapping in 2004, work that was conducted at the Joint Genome Institute in California.

Blaschek also reported on the benefits identifying of operating in continuous rather than in batch mode, and with a gas stripping recovery technology that allows less expensive butanol production without the fouling that might occur with a liquid membrane-based technique. Blaschek has collaborated with industrial and venture capital partners to scale up the butanol fermentation with the current strain of *C. beijerinckii* BA101, examining different substrates (e.g., DDGS and corn fiber) for butanol production, and developing a second-generation strain of the microorganism.

For the version of the process modeled in this report, Nexant referred to the report by Blaschek et al., "Economics of Butanol Fermentation Using Hyper-butanol Producing *Clostridium Beijerinckii* BA101". A type of wet corn milling is the basis of this version of the process, except that the process is simpler than many of the wet corn mills that exist in that only a starch slurry and corn steep liquor are the components used for the butanol fermentation – saccharification is not required with the bacterium used. Batch fermentation is the process used in the case modeled. Total fermentation time is assumed to be 72 hours. The total productivity for ABE (acetone, butanol and ethanol) is 0.38 g/l-hr. The process is shown as a schematic in Figure 3.35.

More recent developments reported by Blaschek et al are for continuous fermentation, stripping solvents from the fermentation medium with CO_2, and condensing to recover the solvents. In such an improved scheme, the solvent ABE yield of the fermentor goes from 17.6 g/l to 460.4 g/l. For reference, note that yeast fermentations producing ethanol operate with ethanol concentrations of 12-17 percent (120-170 g/l).

Background on C. beijerinckii

Some basic facts about *Clostridium beijerinckii* (see Figure 3.36):

- The genus clostridium is very widely found in nature and in industrial fermentation; C. *beijerinckii* species are also found widely in nature and are routinely isolated from soil samples
- Saccharolytic (sugar-metabolizing)
- Strictly anaerobic
- Mesophylic (does best at 10-40 °C)

Figure 3.35 Schematic Flowsheet of Batch *C. beijerinckii* BA 101 Butanol Process

(As modeled in this report)

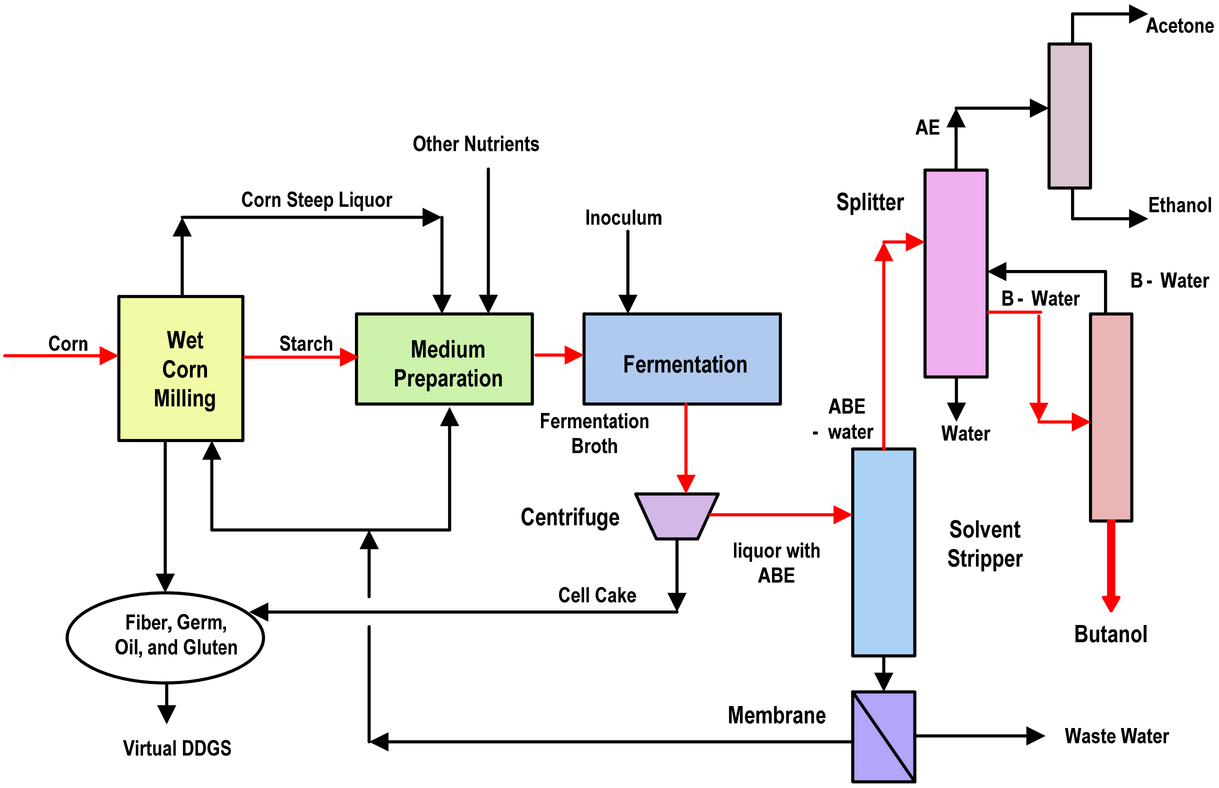
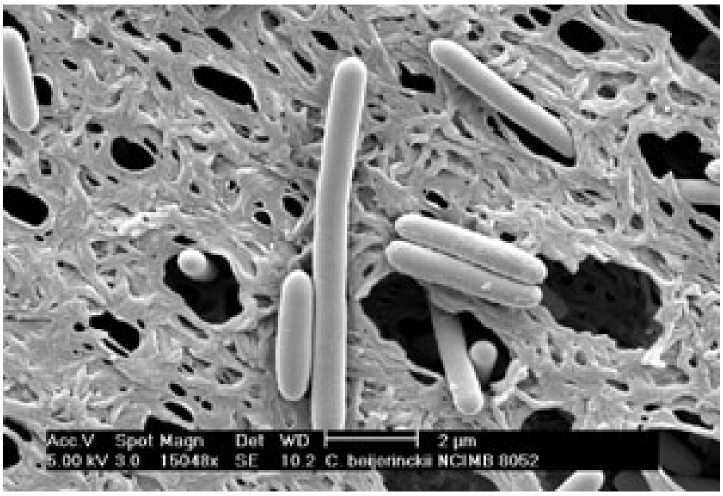


Figure 3.36 Scanning Electron Micrograph of *C. beijerinckii*

(S. Robinson, Imaging Technology Group (ITG), University of Illinois (25600 X))



- Motile (covered all over with flagella), but can be immobilized on porous or fibrous media), rod-shaped bacteria with oval, sub-terminal spores; the form of the cell changes over the growth cycle of the organism:
  - At early rapid growth phase, the cells are long, filamentous and very motile
  - As the culture approaches the solventogenic stage, which corresponds with the stationary phase, cells shorten, become plumper and have less motility
  - In fermentations, *C. beijerinckii* produces a number of products including acetate, butyrate, lactate, hydrogen gas, carbon dioxide, acetone, butanol, ethanol, acetoin and acetyl methyl carbonil

3.2.8 Syngas to Ethanol

Although most corporate efforts and the vast majority of US federal resources have gone towards developing enzymatic conversion, there also has been some good work done on biosyngas fermentation in the US and elsewhere.

The basic chemistry of bacterial fermentation of CO, CO_2, and H_2 to ethanol is shown in Figure 3.37.

Figure 3.37 Bacterial Syngas Fermentation Chemistry

$$6CO + 3\,H_2O \longrightarrow C_2H_5OH + 4CO_2$$

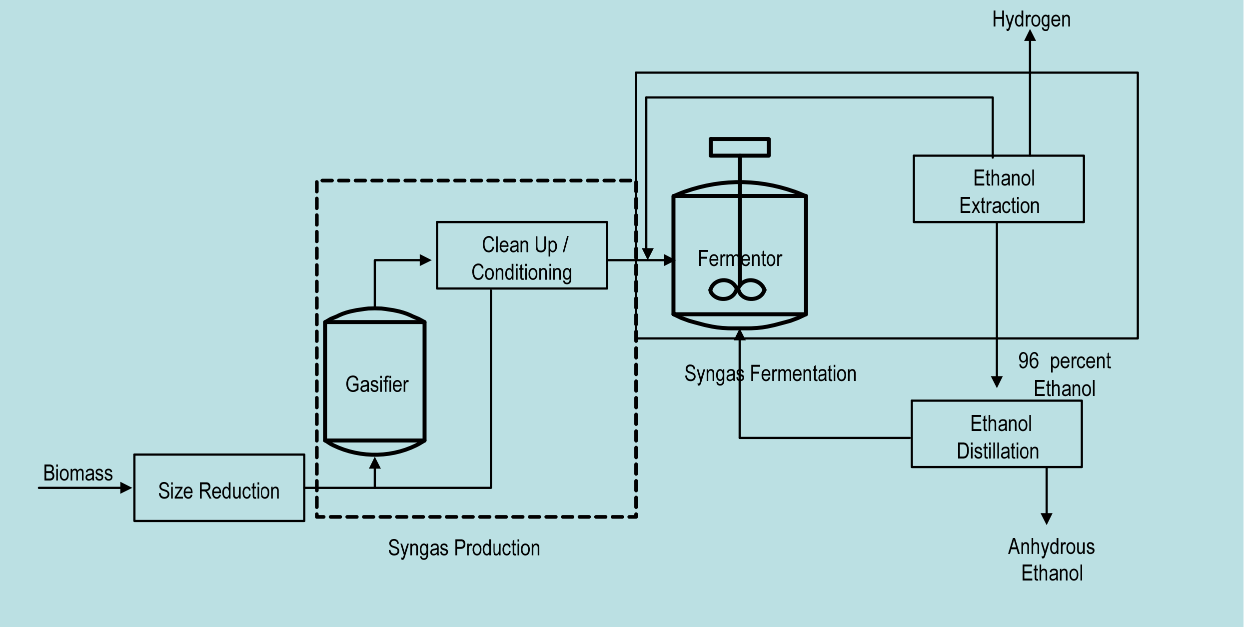
$$6H_2 + 2\,CO_2 \longrightarrow C_2H_5OH + 3H_2O$$

In fermentation, co-production of acetic acid leads to a decreased pH, which inhibits the organisms. To avoid further inhibition the organisms switch to ethanol production. With a syngas H_2/CO ratio of 2, water and ethanol are the only theoretical products, but the ratio is not of major importance as the bacteria prefer CO. CO/H_2 shift reactions to improve the ratio are thus not necessary as they would be in thermochemical catalytic synthesis. Ethanol is toxic to the bacteria, so ethanol concentrations must be held below 3 percent in the reactor.

The biocatalytic reaction has the advantages of high yields and a very high selectivity. The only products are ethanol, CO_2, and water, thus avoiding upgrading, cracking or separating processes for lower grade products.

A typical process schematic is shown in Figure 3.38.

Figure 3.38 Biosyngas Fermentation Process Schematic



Despite the research efforts to date, syngas fermentation strains, and processes apparently remain relatively poorly characterized compared to other routes. There are many other issues to be resolved as well, including:

- Overall process economics
- Achieving performance targets required for viable process economics, for:
  - Gasification
  - Syngas fermentation, e.g., ethanol productivity, yield, titer, and rate

This type of technology, while still unproven, may enable higher yields than fermentation through conversion of non-carbohydrate (e.g., lignin) and/or hemicellulosic fractions to syngas. In addition, the technology can build on gasification and gas cleaning knowledge previously developed or now being developed by others. It also has the ability to process a diverse range of feedstocks to a common syngas intermediate. Entities active in this development include:

- BRI Energy
- Oklahoma State University
- Mississippi State University

Bioengineering Resources, Inc. (BRI) (Fayetteville, AR), or BRI Energy, uses the bacteria Clostridium ljungdahlii (US Pat. #5,173,429). Their technology was piloted in Arkansas, where ethanol was produced from diverse feedstocks for four years. The reaction time from biomass to distilled ethanol was proven to be short (7-8 minutes) compared to fermentation of sugars, with residence times as long as 1-2 days.

3.2.9 Hydrocarbons by Fermentation

3.2.9.1 Solazyme – Microalgae Diesel

Solazyme, Inc. is a synthetic biology company using algae to address biofuel, industrial chemical, and health and wellness markets. The company is developing genetically engineered algae to produce many different oils and hydrocarbons for transportation fuels, with strains appropriate for multiple product areas.

Solazyme implements a microbial fermentation process that allows algae to produce oil in industrial scale vessels quickly and efficiently. Solazyme aims to use various sugar substrates and different non-food feedstocks also, including waste glycerol and sugars derived from various cellulosic materials including wood chips, corn stover, and switchgrass.

Solazyme grows their algae in a classical fermentation regime, in the dark, inside large stainless steel containers instead of in ponds or enclosed in plastic tubes that are exposed to the sun. The organisms convert sugars into biomass and different types of oil. The pressure and other environmental factors inside the vat are managed to promote sugar conversion to oil. The oil can be extracted and further processed to make a wide range of fuels, including diesel and jet fuel, as well as other products. Some of Solazyme's algae strains produce triglycerides (natural oils), while others produce a mix of hydrocarbons similar to light crude petroleum. Figure 3.39 displays a development fermentor used by Solazyme.

Figure 3.39 Solazyme's Algae Fermentor

Source: Solazyme, Inc.

In utilizing lignocellulosic biomass, the component lignin can poison other microorganisms. In common processes, lignin is required to be separated from the sugars to keep the microorganisms healthy, but the tolerance of the algae to lignin makes it possible to leave out this step, which in turn will reduce overall costs.

Other advantages of growing algae in the dark are:

- Keeping the algae in the dark causes them to produce more oil than they do in the sunlight because while their photosynthetic processes are inactive, other metabolic processes that convert sugar into oil become active.
- Feeding the algae sugar makes it possible to grow them in concentrations that are orders of magnitude higher than when they are grown in ponds using energy from the sun because the sugar provides a concentrated source of energy.
- Higher concentrations reduce the amount of infrastructure needed to grow the algae and also making it easier to collect the algae and recover the oil, considerably cutting down costs.

High capital costs have been a major factor retarding other attempts to make fuel from algae.

Solazyme aims to produce fuels that can go right into the refining structure and be competitive with fossil fuel alternatives. The company claims to be capable of producing millions of gallons of biodiesel derived from algae within three years of their 2008 scale up. Solazyme is the first company to generate algae diesel that meets the United States standards. They have released a microalgae derived renewable diesel fuel, Soladiesel, which meets the American Society for Testing and Materials (ASTM) D-975 specifications for petroleum diesel fuels.

Soladiesel is an output from the refinery, wherein a hydrotreatment stage deoxygenates the algal oil, resulting in a hydrocarbon product, with a chemical composition identical to that of the standard petroleum based diesel, compatible with the existing transportation fuel infrastructure in all facets. It has a more desirable environmental footprint than the standard petroleum based diesel with having fewer particulate emissions and the renewable diesel meets the new ASTM ultra low sulfur diesel (ULSD) standards. Solazyme road tested a 100 percent blend of Soladiesel in a factory standard 2005 Jeep Liberty diesel engine vehicle.

In January 2008, Solazyme entered into a biodiesel feedstock development and testing agreement with Chevron Technology Ventures, a division of Chevron USA to work on developing algae optimized to produce oils for use in hydrotreatment at a refinery.

3.2.9.2 Amyris – Jet Fuel, Biodiesel

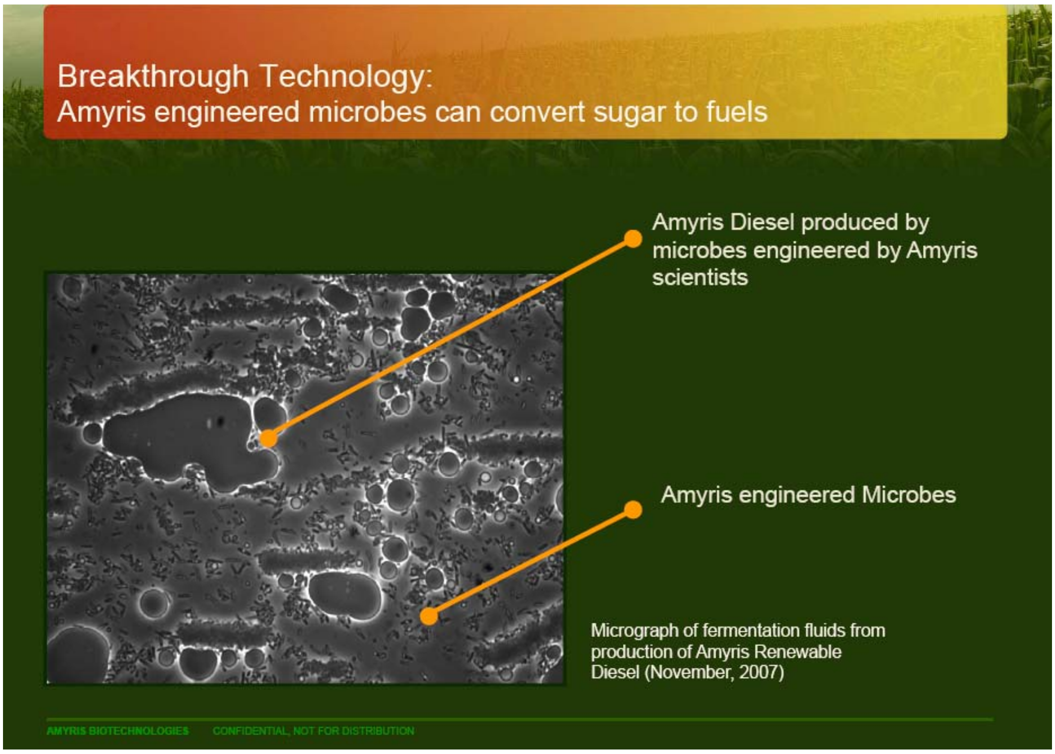
Amyris Biotechnologies aims to develop solutions for major, challenging, and global problems using advances in molecular, cell and systems biology. Their initial focus was to provide affordable anti-malaria drugs to developing economies. Amyris' current focus is to leverage proprietary technology platform to develop drop-in hydrocarbon biofuels.

Amyris is developing a bio-jet fuel that meets or exceeds the ASTM requirements for Jet-A, but with significantly lower emissions. They are also in the developmental stages for producing renewable diesel fuel that can attain lower costs and much greater scale than vegetable oil based biodiesel. It is more stable at colder temperatures compared to conventional biodiesel and it also does not breakdown during storage and transport.

Amyris aims to make their biofuel from the same feedstocks and production plants that are used to make ethanol.

Amyris uses synthetic biology to reprogram microbes. The primary function of the technology (Re: Figure 3.40) was used to reduce the production costs of artemisinin-based anti-malaria drugs. This platform has more recently been used to produce high performing hydrocarbon-based transportation biofuels.

Figure 3.40 Amyris' Technology



Breakthrough Technology:
Amyris engineered microbes can convert sugar to fuels

Micrograph of fermentation fluids from production of Amyris Renewable Diesel (November, 2007)

AMYRIS BIOTECHNOLOGIES CONFIDENTIAL, NOT FOR DISTRIBUTION

Source: Amyris Biotechnologies

The microbial factories ferment sugar to produce hydrocarbons. Figure 3.41 displays the vats used for the Amyris process. The process has considerably less effect on global warming than the traditional fuel production technology. The hydrocarbons produced have the same molecular structure as traditional petroleum fuels therefore their fuels will be compatible with the current infrastructure.

Figure 3.41 Amyris' Pilot Fermentors

Source: Amyris Biotechnologies

Amyris has produced hydrocarbons with properties that compete with the current jet fuel industry standard, kerosene-based jet-A. They aimed to produce a fuel as a jet-A equivalent with more energy and a lower freezing point to allow flights over the poles.

The company is currently trying to develop a large-scale fermentation process for hydrocarbon biofuels from renewable feedstocks that can be blended up to 50 percent with petroleum fuels, and using the existing ethanol mills. Amyris does not plan to license its chemical or fuel products because they feel that selling directly to the customers is the best business model.

Amyris is currently in a joint venture with Crystalsev, one of Brazil's largest ethanol distribution and marketing companies, to produce renewable diesel from sugarcane on a commercial scale by 2010. The companies are preparing to make approximately 1 billion gallons of renewable diesel worldwide within approximately five years once production begins. Based in Brazil, the joint venture plans to employ the local producers and sugarcane mills, where Amyris will be the majority stakeholder providing the fuel production technology, while Crystalsev provides their expertise on the commercialization of the project.

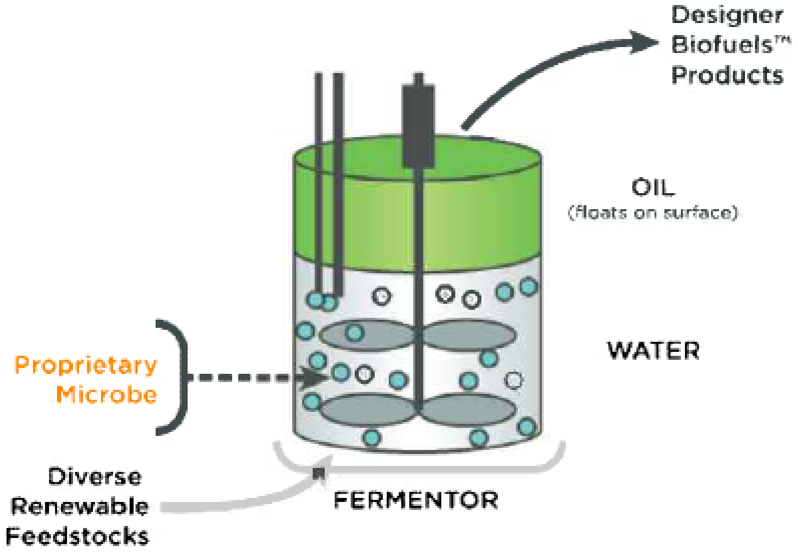
Amyris has another agreement with Santelisa Vale, a majority owner of Crystasev and the second largest ethanol and sugar producer in Brazil. Santelisa Vale is set to supply Amyris with two million tons of sugarcane crushing capacity, and also provide their technical and engineering expertise on the conversion of traditional ethanol plant designs and facilities to Amyris' needs.

On November 11, 2008, Amyris opened its first pilot plant to produce biobased diesel from sugarcane. The pilot plant is located in Emeryville, California and has a 2.4 million gallon capacity, producing just enough for fuel testing, experimenting and securing certification from the United States Environmental Protection Agency (EPA) and fleet operators. The company is planning on opening a second, larger pilot plant in Campinas, Brazil in the spring of 2009 with a targeted commercialization date of 2010.

3.2.9.3 LS9

LS9, Inc. was founded in 2005 and aims to develop sustainable replacements for diverse petroleum products. They have created renewable petroleum designer biocrudes, biofuels, and industrial chemicals from biomass. LS9 has a patented technology with designer microbes, novel processes, and custom product compositions. The technology used by LS9 is a fermentor with proprietary enabling catalysts, processes, and products such as designer: biocrudes, biofuels, and chemicals. A figure of the LS9 technology is seen in Figure 3.42. LS9 has developed industrial microbes, harmless forms of *E. coli* and an engineered strain of yeast, that efficiently convert renewable feedstocks to materials that are compatible with hydrocarbon based fuels and chemicals. Feedstocks can range from any type of agricultural product, from sugarcane to waste, such as wood chips and wheat straw and are converted into fermentable sugars where those sugars are put in a fermentation tank, where microbes are doing the fermenting. The microbes engineered by LS9 were made by lifting genes from other microbes and recombining them into an organism that does what they want, tweaking the characteristics of the fuel desired.

Figure 3.42 LS9, Inc. Technology



Source: LS9, Inc.

LS9 has produced genetically modified microbes, mainly based on *E. coli* organisms (but LS9 is also working with yeast), that utilize a sugar substrate already converted from biomass and to create hydrocarbons (low oxygen biocrude), fatty acid alkyl esters (biodiesel) and various industrial chemicals from sugars by fatty acid biosynthesis. The hydrocarbon products are immiscible and float to the top of the tank where they can be skimmed off. This allows omitting the distillation process and essentially save energy (approximately 65 percent). According to LS9, by slightly altering the microbes, they can make designer biofuels that have the same properties as their fossil fuel based equivalents, such as the biocrude, which can be directly substituted for crude oil, which can be refined into gasoline or used in various petroleum products.

LS9 has developed in their microbes a new way to convert fatty acid intermediates into petroleum replacement products by fermenting sugars more efficiently. They have also found and engineered a new class of enzymes and their associated genes to efficiently convert fatty acids into hydrocarbons. LS9 proposes that this pathway is the most cost, resource, and energy efficient way to produce hydrocarbon biofuels and petroleum replacement products. The LS9 diesel fuel product does not have the carcinogenic benzene and polyaromatic hydrocarbons (PAHs) that the fossil fuel products usually contain. LS9 products also have lower sulfur content than their fossil fuel counterparts. LS9 contends that their renewable petroleum technology is economically viable and has the potential for a fast integration with the existing vehicle fueling systems because their products so closely resemble petroleum fuels.

LS9 has presented some interesting statistics to validate the importance of their more or less drop-in hydrocarbon biofuels:

- There are over 200,000 miles of petroleum pipeline network in the United States; it would cost more than two billion dollars to build a new pipeline connecting the Midwest to the East Coast alone.
- It would cost over five billion dollars to add even one pump for a new fuel to all the 170,000 existing fueling stations
- There are approximately 243 million registered passenger vehicles in the United States, and the replacement lifecycle of the vehicles is over 10 years

The LS9 fuels can be distributed by existing oil pipelines instead of in less fuel-efficient trucks and railcars, can be dispensed in existing gas stations without adding new tankage or special pumps, and the fuels can be used in the current engines instead of modified “flex fuel” engines.

LS9 is developing a pilot scale process to produce their Designer Biofuels by its trademarked Renewable Petroleum process. The company is scaling up their process from the bench scale (1,000 liters-plus) to a pilot scale facility at their laboratory in San Carlos, California. They recently announced an agreement with Crystalsev, a Brazilian sugar and ethanol manufacturer, to begin a joint facility south of Sao Paulo. LS9 will have access to approximately 2 million tons of sugar/year to feed its engineered microbes. They plan to commercially produce an estimated 30 million gallons of diesel fuel as early as 2010, with gasoline and jet fuel production to follow in approximately one to two years after.

The company began small-scale production in 2007 and began pilot operations and engineering for scale up from the laboratory in 2008, along with a design for a demo plant. LS9 plans for the demo plant construction and engineering in 2009 with a design for a commercial plant. In 2010, they propose to have the demo plant in operations with the start of the commercial plant construction. For 2011 and beyond, LS9 is planning on building, owning and operating multiple commercial plants.

3.2.9.4 Others

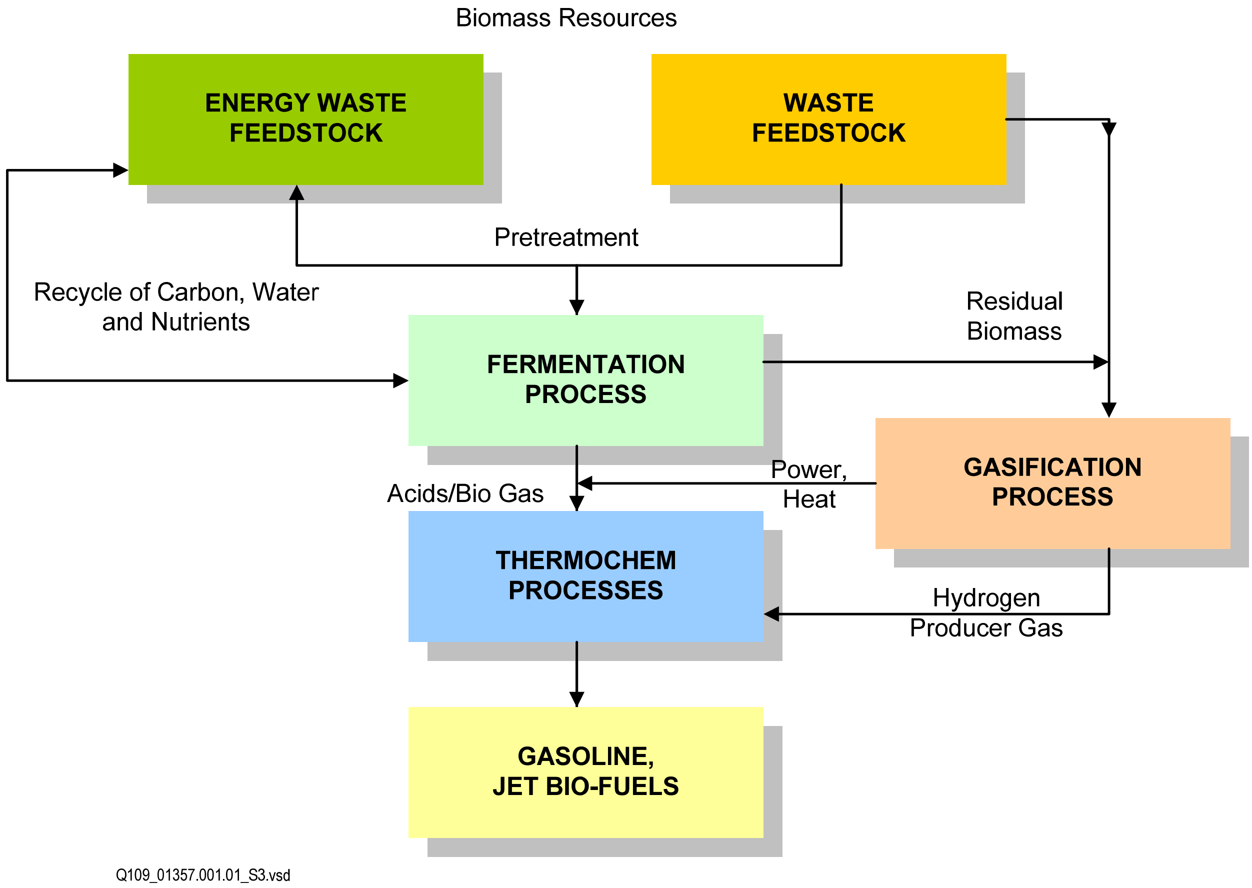
Gevo, Inc.

Gevo, Inc. was formed in 2005 and is focused on the development of advanced biofuels and renewable chemicals based on isobutanol and its derivatives. Their technology allows the production of renewable hydrocarbons, such as isooctane and isooctane, for the gasoline market, renewable jet fuel, and renewable diesel blendstocks. Gevo's technology also enables the production of various chemicals such as isobutylene and paraxylene from renewable sources. Gevo's Integrated Fermentation Technology (GIFT^{TM}) allows for the production of isobutanol and hydrocarbons from retrofitted ethanol plants. One hundred percent of their raw coasts go to a product and they have a low capital cost by combining synthetic biology with chemistry.

Byogy Renewables

Byogy Renewables has licensed the Texas A&M University System processes for the direct conversion of biomass to hydrocarbon fuels such as high octane gasoline or jet fuel. Their preliminary plans are to only produce a 95 octane gasoline fuel with an energy content of 130 thousand Btu per gallon. The proprietary technology by Byogy uses biological fermentation and thermochemical processes created at Texas A&M University. Figure 3.43 shows the process flow diagram of the Byogy process of converting biomass to hydrocarbon fuels. The first two plants are planned to have an output of around five to six million gallons per year depending on the location for the site and the feedstock used. Byogy plans to scale up their processes to have an output of approximately 10 to 25 million gallons per year after a few years of operation. The first plant is planning on using urban waste as the initial feedstock where the plant would grind the waste, sort it, and then convert it to gasoline. Byogy's target is to attain about a two percent contribution to the United States gasoline demand by 2022 by building more than 200 bio-refineries.

Figure 3.43 Byogy Renewables Process Flow Diagram



Source: Green Car Congress: Startup Licenses Texas A&M Technologies for Direct Production of Hydrocarbon Fuels from Biomass; First Product to be 95 Octane Biogasoline, August 19, 2008

3.2.10 Water Usage for Ethanol Production

The most comprehensive methodology for analyzing and quantifying the water usage for a product such as ethanol is life cycle inventory and assessment (LCA). LCA quantifies material and energy flow rates across the entire life cycle of the fuel from cradle to grave. For ethanol, this includes: crop production and harvesting, transportation, ethanol production, and final utilization in a vehicle engine. The two greatest water consumers of these stages are crop production and ethanol production.

The amount of water required to grown corn for ethanol production is dependant on local and regional considerations. In the US, water consumption for corn growing uses approximately 785 volume unit per volume unit of ethanol produced. In China, the water consumption for corn growing per unit of ethanol produced is estimated to be almost 1.5 times that of the US. The greatest concern about water consumption for crop production is competition of water usage. Increase acreage for ethanol corn crops can dip into water reserves for other agricultural processing facilities, livestock operations and even urban living areas. Water consumption in those areas is also on the rise.

Water consumption during ethanol production is much smaller than water consumption for crop production. However, water requirements for ethanol production are still a very significant portion of water demand. During dry mill ethanol production, estimates of water usage range from 3 to 4 volume units of water per volume units of ethanol produced. For example, a 50 million gallon per year ethanol facility can expect to use 150 to 200 million gallons of water per year.

Cellulosic ethanol via biochemical processes is rapidly becoming a viable option for ethanol production. However, water consumption in these kinds of processes is significantly more water intensive with a water to ethanol ratio of 6:1. These processes are not water optimized and have great potential for improvement.

Another option that has evolved is cellulosic ethanol via thermochemical conversion. This kind of process takes steps to reduce the water consumption in ethanol production. For instance, forced-air cooling is used in place of cooling water when possible. The result is a water to ethanol ratio of 1.9:1. Table 3.14 summarizes the overall water demand of ethanol production via corn dry milling, cellulosic biochemical conversion and cellulosic thermochemical conversion. It also gives a breakdown of water usage based on total water consumed in the process.

Table 3.14 Overall Water Demand for Ethanol Production

Fresh Water Demands	Corn Ethanol: Dry Mill	Cellulosic Ethanol: Biochemical	Cellulosic Ethanol: Thermochemical
Cooling Tower Makeup (percent)	68	71	71
Boiler and process makeup (percent)	32	29	29
Overall water to ethanol ratio (H_2O:EtOH)	ranges from 3:1 to 4:1	6:1	1.9:1

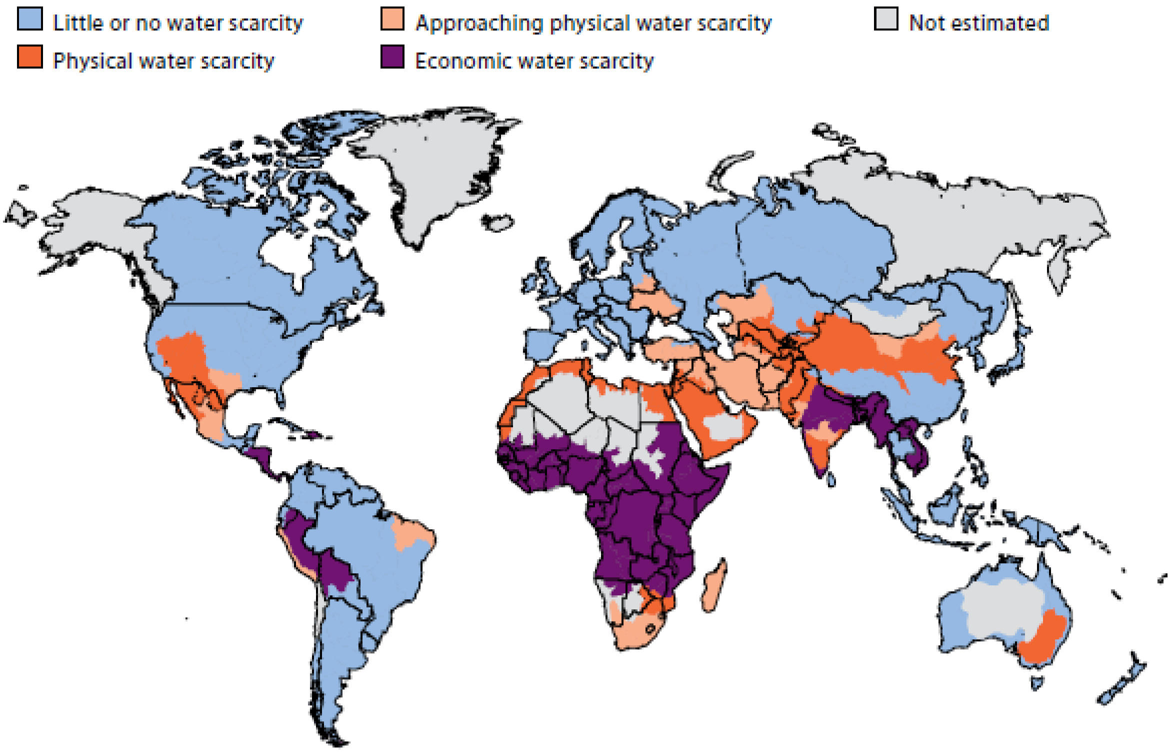
Source: Aden, Andy, “Water Usage for Current and Future Ethanol Production”, NREL, October, 2007.

Energy and water demands of ethanol processes are closely integrated and one way to reduce water demand is to reduce energy consumption. Some options to achieve this include producing broths with higher ethanol concentrations that can reduce the energy needed for distillation. Alternative methods to distillation are being developed, such as pervaporation (a membrane separation process) that can also potentially reduce water usage.

Other methods include utilizing alternative heat transfer mediums, such as forced-air fans for cooling instead of cooling water, as previously mentioned. The use of fans would reduce the mount of water loss to evaporation and blowdown. In the US, the Department of Energy (DOE) is examining water use issues associated with the growth of a biomass to fuels and chemicals industry.

As the world continues to forge ahead in bio-refinery technology development water resource issues will become more important to consider. Figure 3.44 shows the areas of physical and economic water scarcity in the world.

Figure 3.44 Global Water Scarcity Map



Source: International Water Management Institute, "Water for food, water for life: A Comprehensive Assessment of Water Management in Agriculture", February 14, 2007.

Definitions and indicators of the water scarcity map are described in the following:

- *Little or no water scarcity*. Abundant water resources relative to use, with less than 25 percent of water from rivers withdrawn for human purposes.
- *Physical water scarcity (water resources development is approaching or has exceeded sustainable limits*. More than 75 percent of river flows are withdrawn for agriculture, industry, and domestic purposes (accounting for recycling of return flows). This definition, relating water availability to water demand, implies that dry areas are not necessarily water scarce.
- *Approaching physical water scarcity*. More than 60 percent of river flows are withdrawn. These basins will experience physical water scarcity in the near future.
- *Economic water scarcity (human, institutional, and financial capital limit access to water even though water in nature is available locally to meet human demands)*. Water resources are abundant relative to water use, with less than 25 percent of water from rivers withdrawn for human purposes, but infrastructure to supply water is lacking.

Regional variations in water scarcity for some economies like China, India, South Africa, Mexico and the United States are shown in the map. Most APEC member economies fall in regions that do not have a problem with water resources. Member economies such as Peru and

Viet Nam have physical water resources but lack the financial capability to develop infrastructure to properly distribute the water supply. Some areas of northern China and mid-west US have limited water supplies. Overall, however, APEC member economies are in a good position in terms of actual water supply resource based on a very macro economy view. Of course local location of ethanol plants and crop production will affect the water resource supply greatly.

3.3 THERMOCHEMCAL

3.3.1 Pyrolysis for Bio-Oil

Pyrolysis is thermal decomposition occurring in the absence of oxygen. It is also always the first step in processes for combustion and gasification of solid materials, followed by total or partial oxidation of the primary products. Lower process temperatures and longer vapor residence times favor the production of char (charcoal). Higher temperatures and longer residence times increase biomass conversion to gas, while moderate temperatures and shorter vapor residence times are optimum for producing liquids. Product distributions from these different modes of pyrolysis are summarized in Table 3.15. Fast pyrolysis for liquids production is of particular interest because the liquids are transportable and storable.

Table 3.15 Typical Phase Yields from Pyrolysis Modes

(Percent yields, dry wood basis)

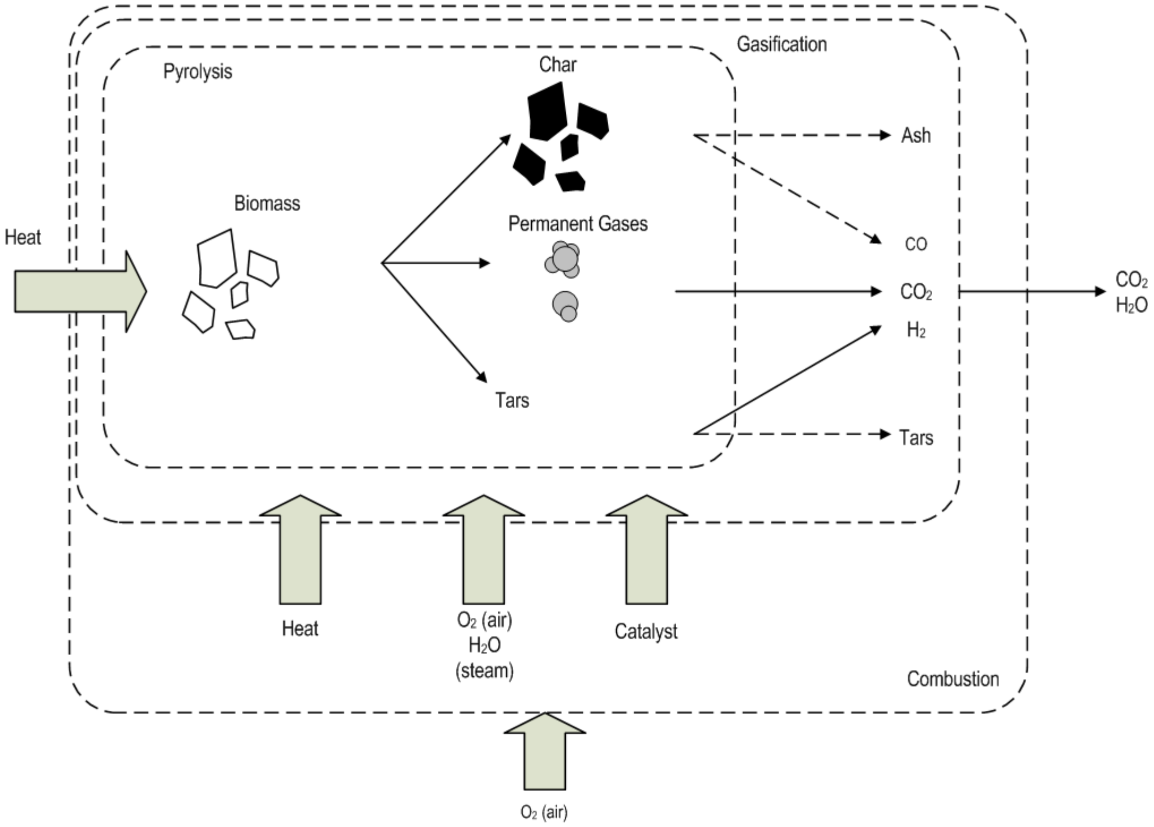
Mode	Conditions	Liquid	Char	Gas
Fast pyrolysis	Moderate temperature, short residence time, particularly vapor	75	12	13
Carbonization	Low temperature, very long residence time	30	35	35
Gasification	High temperature, low residence times	5	10	85

Pyrolysis exists in a continuum with gasification, and was used in earlier eras to make charcoal. Pyrolysis typically operates in the range of 450-750°C, but it also differs from gasification in that it is aimed at directly making liquids (bio-oil) for upgrading, rather than synthesis gas for indirect conversion to liquids. Gases co-produced are generally combusted to supply heat for the endothermic requirements of the process. Figure 3.45 illustrates the centrality of pyrolysis to gasification, where it may be conducted separately, or within the same reaction regime.

Biomass pyrolysis liquids differ greatly from petroleum-based fuels in both their physical properties and their chemical compositions. Pyrolysis liquids generally contain more water and have problems of overall chemical instability, susceptibility to aging, acidity, corrosivity, high viscosity, relatively low calorific value, and they are especially unstable when heated in air. Pyrolysis liquids need to gasified or upgraded or otherwise stabilized soon after they are produced to avoid formation of polymers, gums, and gels. Because of the property and chemistry differences, the standard approaches to processing petroleum fuel oils may not be suitable as such for upgrading biomass pyrolysis liquids.

An alternative to upgrading bio-oil to fuel fractions using hydrogenation, cracking or gasification is the isolation of individual compounds, or exploitation of the chemical character of bio-oil to find applications for the whole oil or its fractions. Bio-oils contain high concentrations of carbonyl, carboxyl, and phenolic functional groups, which suggests various applications as a reactive feedstock.

Figure 3.45 Schematic of the Gasification-Pyrolysis Continuum



Source: V. Swaaij. et al, Thermal conversion of biomass into secondary products. 12th European conference on Biomass and Waste, Amsterdam, 2002.

3.3.1.1 Pyrolysis Technology

Fast Pyrolysis

The most interesting pyrolysis process today is fast pyrolysis, which occurs in a few seconds or less. Therefore, chemical reaction kinetics plays a role along with heat and mass transfer and phase transition phenomena. It is critical to bring the reacting biomass particle as quickly as possible to the optimum process temperature to minimize exposure to the intermediate (lower) temperatures that favor formation of charcoal. One way is to use small particles in fluidized bed processes. Another possibility is to transfer heat very fast only to the particle surface that contacts the heat source, which is applied in ablative processes.

In fast pyrolysis, biomass decomposes to generate mostly vapors and aerosols and some charcoal. After cooling and condensation, a dark brown liquid is formed with a heating value about half that of conventional fuel oil. While it is related to the traditional pyrolysis processes for making charcoal, fast pyrolysis needs carefully controlled parameters to give high yields of liquid. Its essential features in liquid-producing mode are:

- Very high heating and heat transfer rates at the reaction interface, which usually requires a finely ground biomass feed
- Pyrolysis reaction temperature controlled at about 500°C and vapor phase temperature of 400-450°C
- Short vapor residence times, typically of less than 2 seconds
- Rapid cooling of the pyrolysis vapors to give the bio-oil product

Any form of biomass could be used in fast pyrolysis. While most work has been with wood due to its consistency, and comparability between tests, nearly 100 different biomass types have been tested by many laboratories. These tests range from agricultural wastes such as straw, olive pits and nut shells, to energy crops such as miscanthus, sorghum, and switchgrass, forestry wastes such as bark and sawdust, and industrial or municipal solid wastes such as sewage sludge and leather wastes.

Fast pyrolysis requires drying the biomass feed to typically less than 10 percent moisture to minimize the water in the product bio-oil (up to 15 percent can be acceptable), grinding the feed to about 2 mm for fluidized bed reactors, so particles are small enough for rapid pyrolysis, but large enough for solids (char) separation, and quenching and collection of the liquid product (bio-oil).

The process typically yields about 75 percent by weight of the main product, bio-oil, on dry feed basis, together with by-products of char and light gas, which can be used to provide the process heat requirements. There are thus, no waste streams other than flue gas and ash from these combustions.

Most research and development has focused on the reactor even though it probably represents less than 10-15 percent of the total capital cost of an integrated system. Increased attention is on controlling and improving liquid quality, including by improving collection systems. The rest of a pyrolysis plant consists of biomass receiving, storage and handling, biomass drying and grinding, product collection, storage and, when relevant, upgrading.

UOP-Ensyn

UOP and Ensyn have formed a joint venture company to present Ensyn's Rapid Thermal Processing (RTP)^{TM} technology which converts second generation biomass, such as forest and agricultural residues, to pyrolysis oil for use in power and heating applications. The joint venture also plans to continue their research and development efforts more rigorously and to commercialize next generation UOP upgrading technology to refine the pyrolysis oil into transport fuels like green gasoline, diesel and jet fuel. The RTP Ensyn process is a fast thermal process where biomass is quickly heated without the use of oxygen. The biomass is vaporized and next rapidly cooled to produce high yields of pyrolysis oil. It uses a circulating transported fluidized bed reactor system comparable to the one used in the UOP and other Fluidized Catalytic Cracking (FCC) technology. It usually yields about 65-75 weight percent pyrolysis oil from dried woody biomass feedstock where it can then be used for fuel in industrial heat and electricity generation.

Petrobras

It should be noted that Petrobras is similarly pursuing applications of FCC technology to fast pyrolysis/steam cracking of triglycerides (fats and oils) to hydrocarbons, pulverized straw to oils, and ethanol to ethylene.

Genting

The Genting Group, one of Asia's largest conglomerates located in Malaysia, has revealed their Genting Bio-Oil which is Malaysia's first commercially produced bio-oil. The company converts the waste created by Malaysia's large number of oil palm plantations, specifically the empty palm fruit bunches (EFBs) into bio-oil. The bio-oil is made from solid biomass which is left over as waste from the edible vegetable oil which had been extracted. The Genting Bio-Oil technology uses a continuous pyrolysis process (fast pyrolysis) that converts all of the EFBs, approximately 13 million tons produced each year in the economy, to about 3.5 million tons of bio-oil per year. The product can be used in a various applications such as direct co-combustion at power plants and boiler to generate heat and electricity and has the potential to be used as a future replacement for transportation fuels. The bio-oil is carbon neutral and will eventually help lower environmental pollution from GHGs. Genting has teamed up with BTG Biomass Technology Group, a Dutch company, and have completed the first pyrolysis plant in 2005, based on rotating cone pyrolysis technology where the EFBs are converted into fast pyrolysis oil.

Dynamotive Energy Systems

Dynamotive Energy Systems, based in Vancouver, BC, that is one of several companies specialized in fast pyrolysis. The company's fast pyrolysis process heats prepared feedstock in a bubbling fluid bed reactor to 450-500ºC in the absence of oxygen. This is lower than conventional pyrolysis systems and, therefore, benefits from higher overall energy conversion efficiency. The feedstock is flashed and the resulting gases pass into a cyclone where solid particles and char are extracted. The gases enter a quench tower where they are quickly cooled using BioOil already made in the process.

The BioOil condenses and falls into the product tank, while non-condensable gases are recycled to the reactor for process heating. All of the feedstock is utilized in the process.

Dynamotive's Guelph, Ontario plant was the first commercial-scale facility to produce bio-oil from biomass. At full operation the plant can process 66 thousand tons per year of biomass.

Recently, Dynamotive entered into commercial agreement to support the development of a pyrolysis plant in Henan province, China. The plant will be developed by Hubei Xinda Bio-oil Technology Co. Ltd in cooperation with Great China New Energy Technology Services Co. Ltd., which is the exclusive licensor of Dynamotive's technology in China.

Slow Pyrolysis

Slow pyrolysis is another version of the thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen. The feed material is also dried, but instead of being fed to a fast-fluidized bed, it is processed in a stirred, heated kiln or other similar mechanical device, which is not intended to minimize, but to emphasize char formation. As the material passes through the kiln, syngas is evolved and is continuously removed. About 35 percent by weight of the dry feed material is typically converted to a high-carbon char material that is collected on the discharge of the kiln. Biomass feedstock for slow pyrolysis include: poultry litter, dairy manure, agricultural field residues, nut shells, paper sludge, energy crops, DDGS, or cotton trash.

BEST Energies

BEST Energies Inc., a Madison, WI firm with an Australian subsidiary, has developed another slow pyrolysis technology. The syngas they claimed is composed of hydrogen, carbon monoxide, methane, and lower molecular weight hydrocarbons, as well as nitrogen and carbon dioxide. A portion of this gas is combusted as a heat source on the pyrolysis kiln. Another portion is combusted to dry the incoming feed material for pyrolysis, and the net syngas is the net energy output and can be utilized to fuel engines, boilers, or as a feedstock for downstream BTL processes.

The char can also be made into agrichar, carbon filtration media, or pelletized fuel. Mostly however, the charcoal by-product is targeted for use as a soil amendment ("agrichar", or "biochar" to be used to create "Terra Preta") and bio-oil. Because the agrichar does not readily break down, it could sequester for thousands of years nearly all the carbon it contains, rather than releasing it into the atmosphere as GHG carbon dioxide. It is believed that this soil amendment could boost agricultural productivity through its ability to retain nutrients and moisture. Terra Preta is a highly productive type of soil created in the Amazon jungle of Brazil by pre-Colombian native Indians, by incorporation of charcoal.

3.3.2 Torrefaction for Feed Preparation

There are several related, fundamental challenges of using biomass in gasification processes:

- Low energy density, high bulk, high moisture content, and potential perishability (tendency to biologically degrade in storage) make logistics of supplying and storage on-site in a large central plant difficult or uneconomic
- Difficult mechanical properties for handling, grinding and feeding to a thermal process, especially if pressurized
- High moisture and low dry weight heat content reduce gasification thermal efficiencies, especially in competition with (wet) bioconversions

Table 3.16 indicates the relatively low heat content of some leading biomass energy resources, generally due to higher oxygen and/or moisture content, as compared to fossil fuels.

Table 3.16 Average Heating Values of Biomass Fuels and Other Common Fuels

Type of Fuel	Typical Heating Value
Solid and Liquid Fuels	BTU per Pound
Green Forestry Residues	4,500
Mill Residue (hog fuel, typical)	5,500
Mill Residue (sawdust, 6% moisture)	8,500
Agricultural Residues (dry, 15% moisture)	7,500
Dry Animal Manures	6,500
Municipal Solid Waste (MSW)	500
Refuse-Derived Fuels (RDF)	6,00
Coal	*12,000*
Fuel Oil	*19,000*
Gaseous Fuels	BTU per cubic Foot
Landfill Gas (LFG)	490
Digester Gas (Biogas)	620
Natural Gas (typical)	1,000
Methane	*900*
Propane	*2,400*
Note: Fossil fuels are shown in Italics	
Source: RWBeck-Yakima, CA Bioenergy Report, Nov. 2003	

Technologies are available to help overcome these challenges, particularly “torrefaction”, or airless, mild pyrolysis of biomass materials, that can convert them to low moisture solids with much greater heating value, so that they will be also much easier to handle, store, ship and process. Torrefaction is an extension of slow pyrolysis. Typical torrified wood, for example, has a stable moisture level of about 3 percent, mass reduced by 30 percent with smoke-producing agents removed, but with 90 percent of its original energy content retained, at a heating value of approximately 22,560 kJ per kg (9,720 Btu per pound), that is, approaching that of coal. It is friable, that is, it can be easily crumbled or pulverized. This technology is also envisioned as being applied in smaller units to enable bringing biomass out of the field and to a central processing location for thermochemical (but not sugar platform) processing. This type of technology is the first step in the CHOREN Carbo-V stepwise gasification currently being demonstrated in Freiberg, Germany, as well as being used in a number of other similar technologies. This type of technology is expected to be fully commercialized in the next several years, and once it is, it is likely to seriously compete with the sugar platform for both gasoline and diesel substitute biofuel production.

3.3.3 Gasification

3.3.3.1 Overview

Several different approaches can be used to convert solid fuels, including biomass, to liquid fuels of various types and qualities. Depending on the technology and the pressure of operation, the biomass can be fed dry, as water slurries, or as separate components, char, and bio-oil, as resulting from pyrolytic pre-treating. Special cases of biomass waste from processes such as mineral-rich, phenolic “black liquor” from Kraft wood pulping in paper pulp mills, and biopond and primary sludge from water treatment plants, as well as anaerobic digester sludge, also potentially can be gasified by various means. Biomass can also be co-fed with coal, petroleum coke, heavy hydrocarbons, or other hydrocarbons to achieve a mix with a greater average heat of combustion and assure operational stability.

Biomass gasifiers are of several broad types in terms of how the heat provided for the endothermic pyrolysis and gasification reactions:

- Air-blown direct – heat of reaction is provided by partial combustion of biomass
- Oxygen-blown direct - heat of reaction is provided by partial combustion of biomass, but with higher energy because the nitrogen diluents is eliminated
- Indirect (steam reforming with heating via heat exchangers or by circulating hot solids)

However, in terms of mechanical design and reaction regime, there are many more process/mechanical options available:

- Fixed Bed:
    - Counter current updraft - Solid moves down, gas moves up
    - Concurrent - Solid and gas move in same direction
        - Downdraft - solid and gas move down
        - Updraft- solid and gas move up
    - Cross-current - Solid moves down, gas moves at right angles
    - Variations:
        - Stirred bed
        - Two-stage gasifier

- Fluidized Bed
    - Single reactor - Low gas velocity, inert solid stays in reactor.
    - Fast fluid bed - Inert solid is elutriated with product gas and recycled
    - Circulating bed - Inert solid is elutriated, separated, and recirculated; sometimes also referred to as fast-fluidized bed or twin-reactor systems.
    - Entrained bed - Usually no inert solid; highest gas velocity of lean-phase systems; can be run as a cyclonic reactor
    - Twin reactor – Steam gasification and/or pyrolysis occur in the first reactor, char is burned in the second reactor to heat the fluidized medium for recirculation; either can be any type of fluidized bed, although the combustor is often a bubbling fluidized bed.

- Moving Bed
    - Mechanical transport of solids contact; careful design needed to avoid solids carryover
- Other

  - Rotary kiln - Good gas-solid contact; careful design needed to avoid solids carryover
  - Cyclonic reactors - High particle velocities give high reaction rates; similar to fast fluid bed reactors

Biomass gasification is the key enabling technology in converting biomass to either high octane (biogasoline) or high cetane (biodiesel) biofuel products. This approach is also known as "biomass-to-liquids" ("BTL"), analogous to gas-to-liquids (GTL) and coal-to-liquids (CTL). Gasification technologies, and especially oxygen blown and indirect versions, can provide syngas (hydrogen-carbon monoxide mixtures) to synthesis of mostly aliphatic hydrocarbons by Fischer-Tropsch (F-T) catalysts, and/or to synthesis of mixed alcohols by various catalyst technologies. Related biomass gasification developments aimed at only heat and/or power generation are generally less demanding than fuel and chemical-producing end uses.

Though biological approaches to convert cellulosic biomass via fermentation to biofuels are well advanced, also feasible is biomass gasification with syngas fermentation (SF) to various alcohols and particularly, in utilizing CO and producing a H_2 by-product.

Biomass Integrated Gasification (BIG) integrates power generation and downstream synthesis with the gasification technology. When combined with F-T liquids synthesis, it can be called BIG-FT, pronounced, light-heartedly, "bigfoot".

3.3.3.2 Gasification Technologies

Choren Carbo-V – Staged Gasification

CHOREN is a technology development and engineering company based in Freiberg, Germany, with multinational partnering objectives, formed to pursue biomass gasification technology for multiple applications. CHOREN (CHOREN Industries GmbH, Germany) Carbo-V gasification is described as a dry-feed, three phase biomass gasification system. (The name of the company is derived from the components of the words **C**arbon, **H**ydrogen, **O**xygen and **R**enewable). The Carbo-V process is designed to handle variability in biomass properties, low heating value, and other issues to produce syngas. The core of the technology consists of feed preparation and feeding steps, and a three-stage gasification process, including:

- Low-temperature gasification
- High-temperature gasification
- Endothermic entrained bed gasification

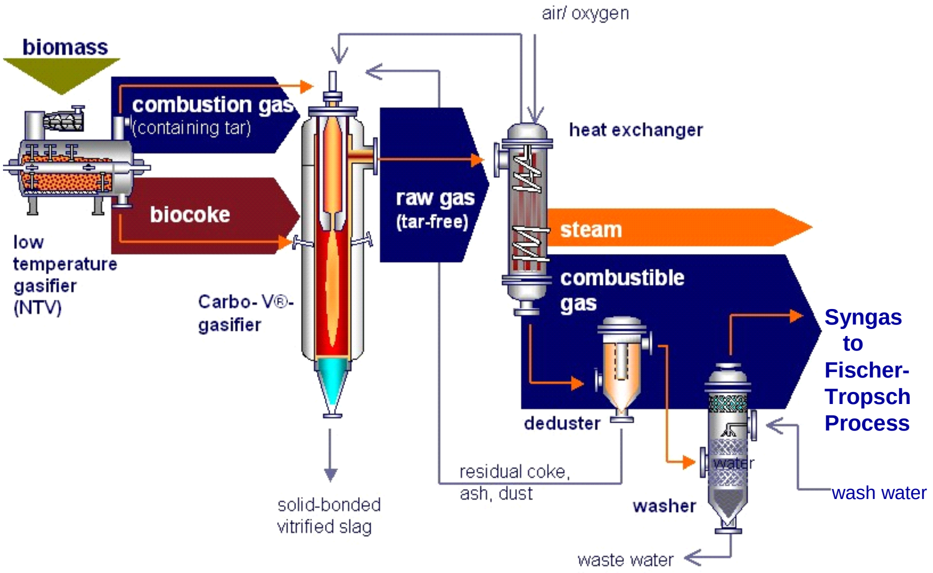
In the low temperature gasification step, biomass (typically with a water content of 15-20 percent) is continually carbonized through partial oxidation (low temperature pyrolysis) with air or oxygen at temperatures between 400 and 500 °C, i.e., it is broken down into a gas containing tar (volatile parts) and solid carbon (char). This step in other contexts is also known as "torrefaction", and can be practiced remotely near the biomass source, to produce materials that are easier to store, transport and further process than is biomass.

In the high temperature gasification step, the gas containing tar is post-oxidized "hypostoichiometrically" (under slightly reducing conditions) using air and/or oxygen in a combustion chamber operating above the melting point of the ash to turn it into a hot gasification medium. The ash quality may be modified as required using additives.

In the endothermic entrained bed gasification step, the char is pulverized and is blown into the hot gasification medium. High temperature and entrained bed gasification are integral steps carried out in stages of the same vessel. The pulverized fuel and the gasification medium react endothermically and are converted into a raw synthesis gas. Treated appropriately, it can be used as a combustible gas for generating electricity, steam, and heat, or as a synthesis gas for producing a Fischer-Tropsch (F-T) sulfur-free diesel fuel substitute.

The CHOREN biomass gasification process is illustrated in Figure 3.46.

Figure 3.46 Process Schematic – CHOREN Syngas Production from Biomass



Source: CHOREN

CHOREN's gasification partial oxidation (POX) is more challenging for biomass than for hydrocarbons because of the oxygen present in the carbohydrate molecules (essentially chains of -CH_2O-), requiring careful attention to overall oxygen balances, as in all or most biomass gasification.

The chemical steps underlying the process are:

- Drying (vaporization of water; T < 200°C)
- Pyrolysis (decomposition of the biomass and tar formation; 200°C < T < 500°C, zone of highest tar formation at 350-400°C)
- Oxidation (oxidation of carbon hydride and hydrogen to cover heat requirement of reaction; 500°C < T < 2,000°C)

- Reduction (reduction of the oxidation products CO_2 and H_2O to CO and H_2; 500°C < T < 1,000°C)

The gasification can be described by the following equilibrium reactions:

$$\begin{array}{ll} 1.\ C + CO_2 & \longleftrightarrow 2CO \\ 2.\ C + H_2O & \longleftrightarrow CO + H_2 \\ 3.\ CO + H_2O & \longleftrightarrow CO_2 + H_2 \\ 4.\ C + 2H_2 & \longleftrightarrow CH_4 \end{array}$$

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As the temperature rises, Reactions 1 and 2 move to the right in the direction of CO or CO and H_2, while Reactions 3 and 4 move to the left in the direction of CO and H_2O or C and H_2.

Relatively pure oxygen is required to produce syngas, but the process can be run in an air-based mode for power generation. Using high oxygen concentrations keeps the volume of the reactors considerably smaller than if air is used, but requires capital and operating costs for oxygen production.

Pearson Technologies, Inc.

Pearson Technologies, Inc. ("PTI"), Aberdeen, Mississippi, has aimed to research, develop, optimize, and commercialize their process for ethanol production, described as a proprietary "reformer" that gasifies biomass in an oxygen-starved environment to produce syngas, which is reacted with a proprietary catalyst in a Fischer-Tropsch synthesis under conditions that produce ethanol with a conversion of greater than 98 percent with, recycle. The history of their process development includes:

- 1989-1995 – Initial pilot plant (400 pounds per hour) work by PTI - gasification of wood waste, bagasse, rice hulls and straw, kennaf, and sewage sludge, etc. to generate syngas
- 1996-1997 - Two years of laboratory scale reactor studies for converting various syngas mixtures to ethanol using proprietary catalysts
- 1999-2001– 30 tons per day development facility tests converting syngas (from methane reforming) to ethanol. Initial results were encouraging; reactor modifications for heat rejection were found to be required
- 2002 to 2007 – Pearson Feedstock Research Inc. formed to further develop "new" feedstocks and provide a pilot scale demonstration of the complete Pearson Process
- 2008-2009 – Currently, Nexant understands that the Aberdeen facility has been shut down and is for sale. It is not clear what the status of any feature of this technology is today.

The manufacturing cost of ethanol utilizing the Pearson Process is projected by Pearson and others studying the process to be between $ 0.50 to $ 0.75 per gallon, depending on facility size, location and cost of feedstock. After reviewing these analyses, Nexant takes exception to some of the assumptions (e.g., feedstock at $30 vs. $15 per ton; $4.00 vs. $1.50 per annual gallon capex). Comparative costs between PTI's process, with Nexant's adjustments, and conventional corn fermentation as modeled by Nexant are presented in Table 3.17.

Table 3.17 Comparative Costs of Ethanol Production – PTI Gasification vs. Dry Corn Mills
(Ethanol Plant (25 million gallons per year))

	Corn to Ethanol[1]	Wood Waste to Ethanol Pearson Process[2], 2007
Utilities	0.17	0.14
Labor, supplies and overhead	0.16	0.16
Feedstock – corn at $4.60 per bushel	1.76	-
Feedstock – wood waste at $45.00 per wet ton	-	0.39*
Other raw materials	0.06	-
Denaturant	0.03	0.03
Total operating costs	2.18	0.72*
Depreciation of capital – 10% per year	0.25	0.40*
Capital Recovery – 10% per year	0.25	0.40*
Total operating cost and capital recovery	2.68	1.52*
Byproduct credit (DDGS at $210 per ton)	-0.59	-
Net cost after byproduct credit	2.09	1.52*

[1] Source: Nexant Model
[2] Source: PTI; * Nexant revisions

This analysis indicates a comparable cost for the Pearson Process ethanol and corn-based fermentation ethanol at a smaller scale than recent corn-based projects. Nexant's revision to the analysis allows a consistent basis for comparison. The conclusions should be valid within the range of uncertainty. Corn and DDGS prices continue to be volatile, but had been essentially going down slowly. Corn prices have gone up recently, and if they stay at the higher level, it should make the Pearson Process and other biomass gasification-based routes to ethanol more attractive than they had been.

Other Biomass Gasification Technologies

A large number of other biomass gasification technologies have been proposed and are being developed worldwide, in Europe, Scandinavia, North America, Brazil, India, China, and elsewhere in Asia and in the world. Many of these are too small in scale, too weakly sponsored, are air-blown, or are so focused on power and heat production as to exclude them as candidates to commercially produce syngas for biofuels production in the mid-term. They therefore do not warrant detailed coverage in this report.

The European Directive on liquid biofuels for the transportation sector has been an important driver to develop new technologies for syngas production aimed at making liquid biofuels using entrained flow gasification. In Freiberg, Germany, three entrained flow gasifiers are in operation for syngas, methanol, hydrogen, and Fisher-Tropsch diesel production from biomass. Pyrolysis oil gasification is also considered as an alternative route for diesel fuel in Europe. CHOREN's Carbo-V, one of them, is discussed above.

Indirect Gasification

There are several versions of indirect gasification in which heat can be transferred from a source burning biomass-derived fuel to a process step which converts biomass or fractions such as char, bio-oil, or gases to syngas, generally in the presence of steam. Heat may be transferred by using a circulated heated, fluidized particulate medium, such as sand, in arrangements that resemble FCC units, or indirectly in enhanced versions of tubular heat exchangers. With the application of steam to the gasification regime, the system is often called “biomass steam reforming”. The TRI development is described below as a salient example of this approach.

- ThermoChem Recovery International, Inc. (TRI).

TRI was established in 1996 to commercially exploit the licensed Pulse Enhanced^{TM} Steam Reforming technology developed by MTCI. Their designs include integrated biomass bio-refinery systems. TRI has developed partnerships with several entities to further develop their technology, including: Brigham Young University; North Carolina State University, University of Utah, US Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE); Center for Technology Transfer, Inc.; American Forest and Paper Association and the Technical Association of the Pulp and Paper Industry (TAPPI).

The TRI system claims the following features:

- High quality, medium calorific value syngas
- Customized syngas composition for downstream processing
- Feedstock flexibility
- Energy self-reliant for the proprietary
- PulseEnhanced™ heat exchangers (Figure 3.48)
- Inherently stable and safe

TRI’s system can be described as steam reforming gasification, which has the following distinguishing characteristics:

- At an elevated temperature carbon will strip oxygen from water to form carbon monoxide and hydrogen
- The endothermic operation uses roughly 20 percent of the heating value of the fuel for the process
- Product gases are hydrogen and carbon monoxide with small amounts of methane, suitable for reforming to alcohols and/or synthetic natural gas

TRI’s patented Pyrolytic Steam Reforming Gasifier (PSRG) features a Staged Temperature Reaction Process (STRP), which is claimed to produce a clean high-Btu syngas from a variety of biomass feeds. A unique feature claimed for the BCT system is that the cyclones and water condenser are integrated and contained within the biomass gasification chamber. This design is said to conserve space and reduce the loss of heat energy.

It is claimed that the First Stage Devolatilization Reactor:

- Forces out the oxygen entrained with feedstock

- In a reducing environment, raises the temperature of the feedstock in three or four distinct stages to just below combustion temperature
- Releases the volatiles (VOCs), which makes their energy available for subsequent reforming or energy production
- Avoids the production of excess heat, CO_2 and other combustion products
- Eliminates "flash pyrolysis" and "run away" combustion
- Eliminates slag and reduces ash production

It is further claimed that the Second Stage Reforming Reactor with entrained flow design that combines feedstock (char) with superheated steam at 1,500ºF, results in:

- Lower operating temperatures within a controlled environment
- Lower soot production partly due to lower maximum temperatures and partly due to higher steam-carbon ratio, which reduces soot production
- Lower emissions: when steam is added as a gasification agent, the H_2 content is increased and the CO_2 content is lowered. This, it is claimed, results in faster combustion and lower emissions of CO and NO_x

The Integrated Gas Cleanup and Conditioning, it is claimed, produces ultra clean syngas with no particulates, tar, or alkali metals, and low NOx, SOx, and CO_2.

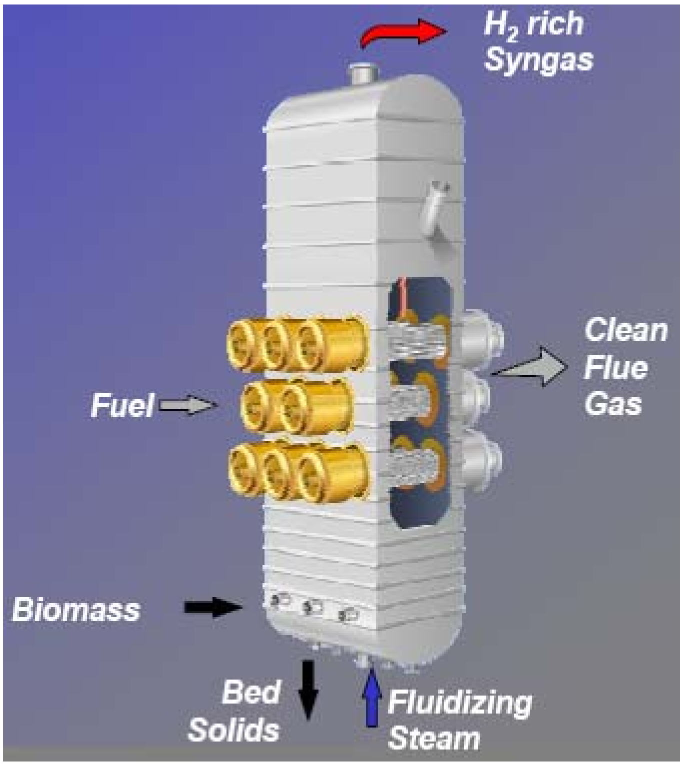
Figure 3.47 shows the Georgia-Pacific, TCI Pulse Enhanced^{TM} steam reforming technology installed and operating in black liquor gasification/chemical recovery in Georgia-Pacific's Big Island, Virginia, containerboard mill.

Figure 3.47 Black Liquor Gasification at Big Island, Virginia

Source: Annual Report 2003 OECD/IEA Implementing Agreement on Advanced Energy-Related Technologies for the Pulp and Paper Industry

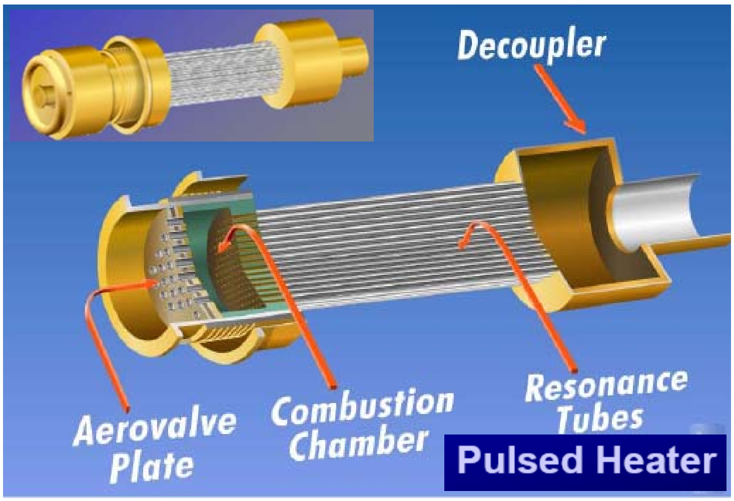
Figure 3.48 shows a schematic of the steam reformer reaction unit, and Figure 3.49 shows a schematic of the pulsed heater, which is the proprietary heart of the process.

Figure 3.48 PulseEnhanced™ Steam Reformer



Source: ThermoChem Recovery International, Inc., 2008

Figure 3.49 Pulsed Heater – Flue Gas Biomass Gasification Heat Transfer



Source: ThermoChem Recovery International, Inc., 2008

3.3.3.3 BTL Diesel/Distillate

Treated appropriately, the syngas from this process can be used as a combustible gas for generating electricity, steam, and heat, or as a synthesis gas for producing a Fischer-Tropsch (F-T) sulfur-free diesel fuel substitute.

The latter application is of primary interest here. However, in the overall plant complex, power and heat would be produced from syngas also. This would be either:

- By burning a part of the syngas in a gas turbine power generation system with a heat recovery steam generator (the "power island"), and perhaps using gas turbine exhaust heat for biomass drying, and/or
- Employing a so-called "once-through" F-T system, wherein unconverted syngas from a single pass through the reaction is used as fuel to the power island

This latter system is modeled in the "BIG-FT" economic analysis presented below in this section.

A more complete discussion of the technology of this process can be found in the Biomass Gasification section above.

Shell is an equity investor in Iogen for establishing a position in fermentation ethanol, but also has entered into a partnership with CHOREN to provide advanced biofuels for both gasoline and diesel engines. Shell is providing the version of its F-T technology used in its Bintulu, Malaysia demonstration plant. Volkswagen is also a partner in the demonstration. F-T technology can also be used to produce higher fractions of gasoline blendstock, or "Top Naphtha", and kerosene (aviation fuel), which is discussed elsewhere in this report.

Carbo-V technology is aimed at F-T production of biodiesel fuel branded "SunDiesel". A 15 thousand ton per year (25 barrels per day) SunDiesel demonstration plant at Freiberg, Germany opened in April 2008.

The Fischer-Tropsch technology has a long history and is well-demonstrated by a number of developers, as indicated in Table 3.18.

Table 3.18 F-T Process History

1902	Methane formed from H_2 and CO mixtures over NI (Sabatier and Senderens)
1923	Fischer and Tropsch report work in CO, Fe, and Ru; at high pressure hydrocarbons are formed
1936	First four production plants in Germany – (200,000 tons >> 700,000 tons in 1944 with 9 plants)
1950	5,000 bpd plant in Brownsville, TX
1950-53	Slurry phase reactor pilot unit developed
Mid 1950s	Decline in F-T plants due to discovery of oil in the Mideast
1955	First Sasol plant commissioned in South Africa; it used Fe catalyst; (1980 and 1983 saw two more plants)
1970-80s	Renewed interest due to energy crisis
1990s	Continued interest fueled by 'stranded' oil reserves
1992	Mossgas' plant uses Sasol technology and natural gas as carbon source
1992-1993	Shell plant (13,000 bpd)uses CO catalyst and natural gas carbon source
1993	Sasol slurry phase reactor (2,500 bpd) using Fe catalyst

Source: Per Nexant and Bukur, D. B. and Sivaraj, C. Appl. Cat. A: Gen. 2002, 231, 201, Dry, M. E. Cat Today 2002, 71,227

Fisher-Tropsch synthesis in a BIG-FT configuration clearly can be designed to produce much more biogasoline (naphtha) than is usual with stranded gas GTL projects. In such configurations, methane-ethane can be burned for process heat and power and for byproduct power for sale at a mid-continental site, and/or reformed to provide hydrogen to the process or, C_2/C_3 can be cracked to olefins if the capacity is sufficient. Wax would be hydro-cracked as usual. Alternatively, C_3-C_4 (propanes-butanes) can be sold as LPG or used as chemical feedstocks. Versions of F-T catalysts are also being developed to produce higher octane gasoline range fractions than the naphtha that is generally produced.

3.3.3.4 Higher Alcohols

Overview

Because there were hardly any incentives for development and significant technical and business risks related to mixed alcohols processes, little commercial development for higher alcohol synthesis (HAS) occurred in the late 1990s and to date. Developers who were early investigators of this technology in the mid-1980s have since abandoned it. New catalysts, new project developers, and a desire to find alternatives for petroleum based-fuels and fuel oxygenates have encouraged renewed interest in mixed alcohols. Much of the renewed interest is from developers of technologies and projects based on exploitation of coal and stranded gas resources through syngas made in coal gasification and /or natural gas reforming processes, but these developments are completely applicable to syngas made from biomass as well.

Much of the discussion in this section is based on work performed by Nexant for NREL in "Task 9: Mixed Alcohols from Syngas: State of Technology", as part of a larger study, "Equipment

Design and Cost Estimation for Small Modular Biomass Systems, Synthesis Gas Cleanup and Oxygen Separation Equipment, Nexant, NREL/ACO-5-44027", which supplements previously reported NREL work in the mixed alcohols section of its 2003 technical report, "Preliminary Screening - Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas, P.L. Spath and D.C. Dayton, December 2003, NREL/TP-510-34929". Unless otherwise noted, data presented in this section is derived from the 2003 NREL mixed alcohols analysis cited above.

The leading catalysts commercially available for mixed alcohol production from syngas are:

- Modified methanol catalysts
- Modified Fischer-Tropsch catalysts
- Alkali-doped molybdenum catalysts

Recent work on zirconium catalysts also shows potential for process improvements.

None of the catalysts investigated appear to be clearly superior to the others. As in other areas of biofuels process development and implementation, process and project developers must examine a range of criteria to determine which catalyst aspects are of greatest importance. While no catalyst appears to have a significant advantage in syngas conversion, molybdenum catalysts performed well on criteria of alcohol yield, selectivity, and impurity resistance. Recent research efforts have focused on changing base catalyst formulations instead of developing entirely new catalysts. These efforts have included doping of catalysts with different metals, novel catalyst preparation techniques, optimizing process conditions, and new catalyst support materials. While many of these research efforts have improved catalyst performance, an evaluation of the economics of each improvement needs to be performed, but such a comparison is beyond the scope of this report.

Technical and economic risks include:

- Feasibility to produce the desired product slate
- Scale-up considerations
- Designing for severe process conditions
- Catalyst sensitivities
- Competitiveness versus petroleum fuels
- Catalyst prices

Studies have shown that current mixed alcohol technologies can compete with wholesale gasoline prices at $1.25 to $1.70 per gallon, assuming $0 per ton feedstock prices and no production credits. Consideration must be given to the impact this product will have on transportation fuel specifications, especially octane, volatility, sulfur, and corrosion. Fluctuations in price for rare and high demand metals also add considerable risk to the commercial feasibility of this process.

Mixed higher alcohols (including mixtures of *n*-butanol and others) can be attractive gasoline blending stocks for octane enhancement, having lower vapor pressure than ethanol or methanol, better solubility with hydrocarbon components, improved water tolerance, and higher overall heating value.

As discussed widely in this report, syngas (CO and H_2 mixtures) can be potentially derived directly or indirectly from biomass, including by gasification (or partial oxidation) of biomass or components, or by reforming methane made by anaerobic digestion of biomass, instead of by reforming or partial oxidation of hydrocarbons.

Depending on the process conditions and catalysts used, large co-product percentages of methanol and CO_2 byproducts may be produced. The first step in HAS is to form methanol, and next to form a C-C bond by inserting CO into methanol (CH_3OH). Linear alcohols are produced in a stepwise fashion by its successive homologation of methanol to ethanol, propanol, butanol, etc. HAS involves a complex set of many reactions with multiple pathways yielding a variety of products limited by kinetic and thermodynamic constraints.

Note that the basic building block of carbohydrates is H-C-OH, or H_2:CO=1:1, and partial oxidation of biomass (carbohydrate) with moisture present adds some hydrogen, but mostly carbon and oxygen. The general HAS reaction mechanism has the following overall stoichiometry (n typically ranging from 1-8):

$$nCO + 2nH_2 \longrightarrow CnH_{2n+1}OH + (n-1)H_2O$$

This reaction stoichiometry implies an optimum H_2/CO ratio of 2.0, but with the water gas shift (WGS) reaction occurring simultaneously, the optimum ratio is closer to 1.0 (that is, CO_2 is formed, taking up the excess oxygen and carbon).

As in other syngas-based processes, a large excess heat of reaction must be removed to control process temperatures, maximize yields, and to minimize catalyst deactivation by potential sintering. HAS is conducted in reactors similar to those in methanol and F-T synthesis processes, and modified methanol and modified F-T catalysts have been the most effective in producing higher mixed alcohols. Again, other types of catalyst under research and development for higher mixed alcohol synthesis include sulfide-based, oxide-based, and rhodium-based.

While other syngas-to-liquid processes have been commercialized (GTL and CTL), commercialization of HAS has been limited by poor selectivity and low product yields.

Increased productivity and improved selectivity in higher alcohol formation is needed for this technology to succeed. Potential improvements could include:

- Injecting lower alcohols in the syngas
- Catalyst beds in series
- Slurry phase reactors

According to the US DOE report cited above (Spath et al), Nexant's study, as well as several others, has evaluated the economics of higher alcohol synthesis from natural gas. Depending on the cost of the natural gas and the economic assumptions used, the results of these studies vary from about \$0.50 to \$1.20 per gallon. The use of biosyngas, where the feed is lower in cost or yields a tipping fee could make these alcohols highly competitive with petroleum gasoline blendstocks.

Sulfur poisoning catalysts is a major concern of HAS technology based on coal gasification or natural gas reforming. With biomass, however, sulfur content tends to be very low relative to these other resources. Table 3.19 shows the typical sulfur content of some major biomass resources and in the untreated emissions from combustion of the same, if not absorbed in part by ash. This defines a range of 100-1,000 ppm, which will be roughly reflected in the concentration in the syngas.

Table 3.19 Sulfur Content of Biomass Types

Biomass Type	Sulfur, %	Sulfur Emission LB/MM Btu
Hardwood	0.03	0.036
Debarked pine	0.01	0.011
Switchgrass	0.1	0.125

The tolerance of modified methanol and Fischer-Tropsch catalysts to sulfur is very low (<1 ppm). Sulfided catalysts represent an improvement in this area. If a system is required to maintain between 50 and 100 ppm of sulfur in the syngas, only very small improvements in the overall process economics are possible. In addition, low sulfur requirements, especially for H_2S and mercaptans for transportation and chemicals applications of the mixed alcohol products, may require additional cleanup anyway, potentially eliminating any economic advantage.

Technology Overview

In the early 1980s, chemical companies such as Dow and Snamprogetti patented their own higher alcohol synthesis technologies in response to the oil embargo of the 1970s and the phase-out of tetraethyl lead as an octane enhancer in gasoline. However, commercial interest decreased with the increased supply of cheap petroleum and the use of methyl tert-butyl ether (MTBE) as an octane booster. With excellent blending properties and good economics, MTBE became the primary oxygenate chosen by refineries outside of the Midwest to meet the reformulated gasoline standards of the Federal Clean Air Act Amendments of 1990. The proceeding phase-out of MTBE from the gasoline pool has substituted ethanol and renewed interest in mixed alcohols as an alternative oxygen octane sources. As of mid-2006, no commercial plants exist that solely produce mixed alcohols in the C_2-C_6 range from syngas. Many of the companies that had once pursued research to commercialize the production of mixed alcohols have now abandoned it.

The main steps in HAS are:

- Synthesis gas production

- Gas clean up and conditioning
- Alcohol synthesis
- Product purification

This is a typical route regardless of how the syngas is used. Items unique to mixed alcohol production are the process conditions for product synthesis, level of clean up (depending on the catalyst chosen), and purification/recycle steps. It is worth mentioning that Sasol has commercial plants in South Africa that utilize the mixed alcohol by-product of their coal-to-liquids (CTL) process for other commercial needs. However, these plants are not optimized for mixed alcohols production, and, thus, do not qualify as commercial plants for the same.

Higher alcohol synthesis catalysts have undergone a number of improvements in the past few years. The majority of the incremental improvements relate to better characterization of higher alcohol yields for different catalyst compositions. In addition, potentially significant improvements in yields have come from research on new catalyst formation processes. The additional work that has been performed on mixed alcohol catalysts requires new categorization. Three of the four categories remain the same as in the NREL 2003 technical report.

The categories are as follows:

- Modified high pressure methanol synthesis catalysts - alkali-doped ZnO/Cr_2O_3
- Modified low pressure methanol synthesis catalysts – alkali-doped Cu/ZnO and $Cu/ZnO/Al_2O_3$
- Modified Fischer-Tropsch catalysts – alkali-doped CuO/CoO/ Al_2O_3
- Alkali-doped molybdenum based catalysts
- Other catalysts, mainly ZrO_2 based

If some of the new research continues to yield improvements and advances over existing catalysts, it may be possible for molybdenum-based catalysts to be more active than oxide-based catalysts if prepared under new methods. Nexant has recommended that NREL follow closely to assure the most up-to-date data is included in mixed alcohol designs.

Modified High Pressure Methanol Synthesis Catalysts

Modified high pressure methanol synthesis catalysts are primarily alkali doped ZnO/Cr_2O_3. The typical process conditions are summarized in Table 3.20. Unless otherwise noted, data for process conditions tables are derived from the 2003 NREL mixed alcohols analysis cited previously.

Table 3.20 Modified High Pressure Methanol Catalysts Process Conditions

H_2/CO Ratio	Temperature (°F)	Pressure (psia)	CO_2 Sensitivity	CO Conversion (per pass)	Mainly Product Yield	Total Alcohol STY (g/kg$_{cat}$)/hr
1	572-800	1,810-3,625	Significant @ 6%	5-20%	Branched primarily Alcohols	203[3]

The benefits of these catalysts include:

- Significant data available to predict the performance and effectiveness of Zn/Cr catalysts
- Highest iso-butanol production rates of any catalyst group

The drawbacks to these catalysts include:

- Significantly decreased C_2+OH yields with CO_2-rich (~6 percent) syngas stream
- High pressure requirements

Roberts et al at North Carolina State University has published research dealing with isobutanol synthesis from such ZnCr catalysts. This work is directed towards the use of ZnCr catalysts for HAS in slurry reactors to increase selectivity and yields of higher alcohols, but no such improvements were reported in 2005.

Modified Low Pressure Methanol Synthesis Catalysts

These are alkali-doped Cu/ZnO and $Cu/ZnO/Al_2O_3$ system, such as the Lurgi Octamix process (w/Süd Chemie, providing the catalyst).

The difference between modified high pressure and modified low pressure methanol synthesis catalysts is that the latter formulation contains copper. The typical process conditions are summarized in Table 3.21. The ranges given cover the conditions under which most catalysts of this type would operate.

Table 3.21 Modified Low Pressure Methanol Catalysts Process Conditions

Catalyst	H_2/CO Ratio	Temp. (F)	Pressure (psia)	CO Conversion (per pass)	C_2+ Alcohol Selectivity
Lurgi Octamix	1-1.2	482-752	725-1,450	20-80%	41.9 wt %

The benefits of these catalysts include:

- Lower pressure requirements than high pressure methanol catalysts
- Effectiveness of process has been detailed in the literature

The drawbacks of these catalysts include:

- High CO conversion can decrease higher alcohol selectivity and yield
- Lower production of higher alcohols and other oxygenated products than modified high pressure methanol synthesis catalysts
- Cu sintering limits the upper temperature of the process

NREL's 2003 technical report mentions that modified low pressure methanol catalysts mainly produced primary alcohols. In addition, the literature indicates that modified low-pressure methanol synthesis catalysts also significantly produce branched primary alcohols. Specifically, K-promoted/Cu/ZnO/Al_2O_3 catalysts fall into a group of catalysts that predominantly produce branched alcohols, such as isobutanol. This is particularly important for understanding the mixed alcohol product composition produced by this catalyst.

In addition, recent research conducted by Ismail Boz of Istanbul University has improved the understanding of modified low pressure methanol catalysts with Co and K. The research found that a 5 percent K_2O Promoter concentration yields the greatest higher alcohol selectivity for a Co_2O_3/CuO/ZnO/Al_2O_3 catalyst, and that 563 K maximizes higher alcohol selectivity over methanol with an $H_2/CO = 2$ at 580 psia. In addition, using lower space velocities than those used for methanol synthesis can improve higher alcohol selectivity, and, increasing CO conversion beyond 10 percent, which is shown to be dependent on temperature, reduces higher alcohol selectivity and yield in favor of hydrocarbons. Thus, in order to increase higher alcohol selectivity and yield with a modified low pressure methanol synthesis catalysts, it will be necessary to lower the space velocity and to use the correct amount of promoter. In addition, it is important to recognize that there may be a trade off between maximizing CO conversion and maximizing the higher alcohol selectivity and yield.

Modified Fischer-Tropsch Catalysts

Modified F-T catalysts consist of alkali-doped CuO/CoO/Al_2O_3 systems. Most of the earlier information on the modified Fischer-Tropsch catalyst originated from the commercial process developed by the Institut Francais de Petrole (IFP) over 15 years ago. There have, however, been recent independent developments related to new catalyst preparation techniques. The general process conditions are summarized in Table 3.22. Depending on the type of alcohols desired, H_2/CO ratio, temperature, and pressure can all be manipulated to promote heavier or lighter alcohol production.

Table 3.22 Modified Fischer-Tropsch Catalyst Process Conditions

Catalyst	H_2/CO Ratio	Temp. (F)	Pressure (psia)	CO Conversion (per pass)	C_2+ Alcohol Selectivity	Primary Product Yields
IFP	2/1	500-608	850-1,450	5-30%	30-50%	Straight-chained alcohols

The benefits of these catalysts include:

- Greater selection for higher linear alcohols than modified methanol processes
- New catalyst preparation techniques can significantly improve CO conversion rates

The drawbacks of these catalysts include that decreasing H_2/CO ratio increases higher alkane yield. This should not be an issue with biomass, which tends to have a high H_2/CO ratio. Different catalyst preparation techniques have shown different conversion rates for the syngas feed. The typical method of catalyst preparation has been co-precipitation. However, alternative techniques for catalyst preparation have been shown to increase overall conversion rates. For example, researchers have recently claimed that preparing catalyst with the sol-gel/oil-drop method can increase CO conversion rates by approximately 14-30 percent over catalysts prepared by co-precipitation methods. This has important implications when considering the maximum yield of mixed alcohols expected from a given modified Fischer-Tropsch catalyst.

Work by Dantas de Aquino (Brazil, 2001) helped characterize the effect of alkali metals on the higher alcohol yield and selectivity of Al-Cu-Co based catalysts. Specifically, Li, Na, K, and Cs were tested and the following was found:

- Li increases selectivity of methanol and ethanol yield, while decreasing that of hydrocarbons
- Na increases catalyst deactivation, while the selectivity of hydrocarbon and alcohol remains relatively constant
- K reduces overall higher alcohol yield and produces only methanol and ethanol. It also reduces hydrocarbon yield
- Cs considerably lowers alcohol yield selectivity

These results should be considered if a modified Fischer-Tropsch catalyst is used. From the current research, it appears that among the available alkali promoters, using Li would have the most beneficial effect on alcohol yield and selectivity.

Alkali-Doped Sulfides, Mainly MoS_2

The category of alkali-doped sulfide catalysts as discussed herein includes all molybdenum-based catalysts, divided between sulfide molybdenum-based catalysts and pre-reduced catalysts.

Note that this expands the coverage of this catalyst type in NREL's 2003 analysis. Table 3.23 summarizes the basic process conditions for sulfide catalysts.

Table 3.23 Alkali-Doped Molybdenum-Based Catalysts Process Conditions

Catalyst	H_2/CO Ratio	Temp. (ºF)	Pressure (psia)	CO Conversion (per pass)	C_2+ Alcohol Selectivity	ROH Selectivity	ROH Yield (g/kg cat./hr)
General Literature	1	500-662	435-2,538	10%	75-90%		
Dow				<40%			
K-Co-MoS_2	2	581	1,515	39%		75.70%	115
K-Co-Mo/Al_2O_3	2	650	1,515	-		59%	370
K-Co-Mo/SiO_2	2	482	725	7.20%		59%	370

The benefits of these catalysts include the following:

- The sulfide-based catalysts require 50-100 ppm H_2S in the syngas stream to maintain the sulfidity of the catalyst. Thus, they are sulfur resistant, and sulfur clean up costs may be reduced
- The catalysts appear less sensitive to CO_2 in the syngas stream than other catalysts. However, catalyst activity can still be inhibited with high amounts of CO_2 (>30 percent)
- Coking does not become a problem even with low H_2/CO ratio (e.g., <2)
- Primarily produce non-branched linear alcohols

The drawback is that oxide-based catalysts tend to be more active than these sulfide-based catalysts.

Molybdenum-Sulfide Catalysts

- Catalyst Characteristics

Important research has been recently conducted on alkali-doped sulfide catalyst for higher alcohol synthesis. The sulfide-based catalysts have been better characterized, and the new developments may enable increased higher alcohol yields. For example, when K and Cs are used as promoters on a Co-MoS_2/clay catalyst, the alcohol yield was found to increase with reaction temperature. However, alcohol selectivity decreased with an increase in reaction temperature.

Further developments have characterized the effect of alkali promoters on the yield and composition of C_2+alcohol. The space-time yield of C_2+alcohol was strongly correlated with the alkali metal promoter to MoS_2 ratio (M/MoS_2). The maximum space-time yield was found to be at a maximum around an M/MoS_2 ratio of approximately 0.2 independent of the alkali metal promoter chosen. Of the alkali metal promoters chosen (M: K, Rb, and Cs), the Rb/MoS_2 catalyst with an Rb/Mo ratio of 0.25 demonstrated the highest space-time yield of C_2+alcohol, and it also had the highest chain growth probability, 0.35. Finally, it was found that MoS_2

catalysts could achieve higher alcohol yields than Cu based catalyst, but it requires pressures greater than 1,450 psia.

- Catalyst Formation

Novel developments in catalyst formation techniques have contributed to potentially significant improvements in higher alcohol synthesis yields. The traditional way to prepare MoS_2 catalyst is thermal decomposition or reduction of (NH_4) $2MoS_4$ (ATTM), where ATTM refers to ammonium tetrathiomolybdate. However, recent techniques have been identified that could increase the surface area of the catalyst significantly by preparing the catalyst by the reduction of ATTM in the presence of water. The technique involves the presence of a long chain alkane, tridecane, to increase the surface area of MoS_2 by nearly a factor of four, increasing catalyst activity.

Pre-Reduced Molybdenum-Based Catalysts

- Catalyst Characterization

Much work has also been done on pre-reduced molybdenum-based catalysts. For example, a Mo-Ni-K/SiO_2 catalyst was found to perform better than other pre-reduced molybdenum-based catalysts as measured by largest space-time yield. Additional work on a similar Mo-Ni-K/SiO_2 catalyst demonstrated that space time yield of alcohols could be further increased with a novel method of catalyst formation known as Metal Oxide Vapor Synthesis (MOVS). Given the promise of Mo-based catalysts, the Division of Fossil Energy under US DOE's NETL has recently sponsored work on higher alcohol synthesis from Mo-based catalyst.

Recent DOE-sponsored research on calcined Mo-Ni-K/C catalysts has helped characterize the higher alcohol synthesis that can be achieved with this catalyst. Four major areas of interest were elaborated upon by this research:

- The space-time yield of both alcohols and hydrocarbons are increased with an increase in reaction temperature; however, this causes an overall decrease in total alcohol selectivity as temperature increases
- Addition of Ni and K increases the total alcohol selectivity, but the catalysts must, in general, be reduced first
- Alcohol yield decreases with increasing partial pressure of H_2 and increases with greater partial pressures of CO
- Increased gas hourly space velocity (GHSV) is favorable for total alcohol yields

The general trends of the Mo-Ni-K catalyst supported by carbon are very similar to that seen in molybdenum-sulfide catalysts already discussed. The information obtained by this research helps establish the process conditions - H_2/CO ratio, GHSV, temperature - and catalyst composition that will optimize higher alcohol yields and selectivity for the desired product slate. Catalyst formation and support research has also been conducted on the catalyst support structure and preparation for molybdenum catalysts. For instance, higher catalytic activity resulted from a Mo-K catalyst supported by activated carbon compared to a Mo-K catalyst supported by Al_2O_3.

This research also revealed that the space-time yield of alcohol synthesis is optimized at MoO_3 loading of 48 percent.

Similar to the research on sol-gel preparation techniques for modified Fischer-Tropsch catalysts, the effect of sol-gel preparation of a K-Co-Mo/C catalyst was also studied. The sol-gel method was shown to produce a high alcohol yield, particularly for C_{2+} alcohol.

An additional area of potential interest is the effect of metal doping. In one study, the addition of rhodium as a promoter to a Mo-K/γ- Al_2O_3 catalyst nearly tripled the space-time yield of higher alcohols from 370 to 1,100 g/(hr-kg) of catalyst.

Additional work characterizes the increased alcohol selectivity that K doping has upon a Mo/AC (Activated Carbon Supported) catalyst. These results could possibly increase the attractiveness of sulfide-based catalysts that are promoted by rhodium and potassium. However, rhodium has previously been optimized for ethanol synthesis only, and it is much more expensive than potassium.

Other Catalysts

- Other Sulfide Based Catalysts

There are a variety of other catalysts that have some use in producing higher alcohols, but they are not given much attention because their overall selectivity for higher alcohols has historically been low or they have been developed for other end products. For example, rhodium based catalysts were briefly mentioned in the 2003 technical report as such a catalyst group, yet they are more capable of yielding ethanol than being effective for higher alcohol synthesis.

- ZrO_2 Catalysts

Another new catalyst type is the ZrO_2-based catalyst. A ZrO_2 based catalyst, promoted by Pd, has proven effective for producing ethanol or isobutanol. A study also demonstrated that adding methanol or 1-propanol into the feed of the reactor can increase isobutanol yields by 17 percent and 72 percent, respectively. Representative process conditions are contained in Table 3.24.

Table 3.24 Alkali-Doped ZrO_2-Based Catalysts Process Conditions

Catalyst	H_2/CO Ratio	Temp. (ºF)	Pressure (psia)	CO Conversion (per pass)	ROH Selectivity	ROH Yield (g/ml/hr)	Primary Products
K-PdCuMnZrO_2	9	608-671	1,740	22.6-29.3 mol %	37.7-51.7	41-81	71.3-88.4 wt % CH_2OH
Li-PdZrO_2	2	752	1,160	7-8%		146.3 g/kg/hr	

Reactors

Standard fixed-bed reactors are currently employed in HAS systems. Investigations have been made into two novel processes - multiple reactors and slurry reactors - to improve system performance. While neither of these is commercially available, the discussion below provides an update on both technologies.

- Multiple Reactors

Because HAS is an extremely exothermic process, there is interest in optimizing heat removal. A multiple reactor design, or a "double bed" configuration, is one idea explored to accomplish the process. In this configuration, methanol production from syngas can be optimized in the first bed with a Cu catalyst and low temperatures, and the higher alcohol synthesis yield can be maximized in a second reactor with a higher temperature and a non-Cu Zn-chromite based catalyst.

Promising work on optimizing a double-bed reactor design has been conducted at Lehigh University. The first reactor was optimized for the production of short-chain alcohols over a Cs-promoted $Cu/ZnO/Cr_2O_3$ catalyst, and the second reactor was optimized to synthesize isobutanol over a Cs-promoted ZnO/Cr_2O_3 catalyst. The synergy of these two tubular bed reactors increased isobutanol production by 62 percent above what could be obtained with two reactor beds with the Cu catalyst alone (US DOE, 2003). Research was halted in 1996 because the process was not considered economically promising at the time.

- Slurry Reactors

Using slurry reactors is considerably interesting for higher alcohol synthesis, because, again, the formation of higher alcohols is extremely exothermic, requiring significant heat removal. Breman conducted earlier research of higher alcohol synthesis in slurry reactors compared to fixed bed reactors. His work demonstrated that n-octacosane (a type of paraffin crystal) used as a slurry liquid lowered higher alcohol to methanol selectivity and increased hydrocarbon yields (Breman, B.B., 1995). Over the past decade, the Roberts group at North Carolina State University has conducted a significant amount of research on alcohol synthesis in high temperature (650 K) and slurry bed reactors with a ZnCr catalyst (Sun, Xiaolei, 2001). They have utilized three different slurry liquids for testing:

  - Tetrohydroquinoline (THQ)
  - Tetrahydronapthalene (Tetralin)
  - Decahydroquinoline (Decalin)

This could be interesting for the future if significant breakthroughs can be made, but too little data is currently available to make this a practical current choice for higher alcohol designs.

Technology Developers

The development of a commercialized higher alcohol synthesis process has not significantly changed since the 2003 NREL report cited above, for which Nexant was involved in the follow-up studies for DOE also cited above. No commercial plants have been built, and no pilot plants have been funded. In fact, there appears to have been a decrease in interest by technology developers to further advance HAS technologies. The major developers are discussed following.

- Snamprogetti (or SEHT – Snamprogetti, Enichem, and Haldor Topsoe)

In the 1980s, Snamprogetti and Haldor Topsoe jointly developed a HAS process known as MAS (Metanolo piu Alcoli Superiori – methanol plus higher alcohols). The process was similar to a high pressure, high temperature methanol synthesis process, with the drawbacks of the modified methanol catalysts supposedly avoided. They started a 12 thousand ton per year pilot plant in 1982, and they sold the alcohol mixture as a 5 volume percent blend in a gasoline called SUPER E. Despite the initial interest and promise, the MAS process is no longer available from these companies for the production of mixed alcohols.

- Dow Chemical

While Dow was one of the first to develop and advance HAS technology, it is no longer pursuing the commercial development of their mixed alcohols process. In 1997, they offered to sell their patents for their Sygmal mixed alcohol production process to Power Energy Fuels, Inc. (PEFI) PEFI did not buy the patents, and subsequently, the patents have expired. PEFI is currently attempting to commercialize a modified version of Dow's technology. Dow is no longer involved.

- Lurgi

Lurgi developed their HAS process, known as Octamix, with a low pressure methanol synthesis process in the 1980s and early 1990s. The process tended to yield higher alcohols, and 2 ton per day demonstration plant was built in 1990. A number of divisions within Lurgi were contacted by the Nexant team to determine the current status of the Lurgi technology and interest in the mixed alcohol process. Information from the head of Business Development for Ethanol was not available at the time.

- Institut Francais de Petrole (IFP)

The latest development in IFP's commercial mixed alcohols process occurred when they built their 20 bpd pilot plant in Chiba, Japan. Since that time, they have not ventured forth with any new units. In fact, according to their Strategic Marketing division, IFP has not furthered their work since they built the pilot plant, and they have no commercial interest in pursuing a mixed alcohols process.

- PEFI - Ecalene^{TM}

The Ecalene™ mixed alcohol process continues to be developed by Power Energy Fuels, Inc, (PEFI) based in Lakewood, Colorado, in conjunction with the Western Research Institute (WRI). The process is a modification of Dow's Sygmal process using its polysulfite catalyst. Currently, the process has not moved beyond the bench scale, and the planned 500 gallon per day pilot plant is no longer being pursued. However, there are 2-3 other pilot plants under funding consideration that would produce mixed alcohols from various biomass sources, such as tires, wood chips, and refuse-derived fuel (RDF). One of the pilot plants in consideration is a 2 thousand gallon per day pilot plant at the Wabash River Coal Gasification facility in conjunction with ConocoPhillips. PEFI management predicted that the Ecalene™ process is ready for commercialization, and can produce 1 gallon of mixed alcohols per 270 SCF of syngas.

- Standard Alcohol - Enviroiene^{TM}

The Standard Alcohol Company of America currently has a bench scale process to produce a mixed alcohols product known as Envirolene^{TM}, composed of methanol through octanol. Approximately 50 percent of the product is ethanol, but a more detailed breakdown of its composition is not available due to its proprietary nature. The process uses a modified high-pressure methanol synthesis catalyst. The company is currently seeking funding for a pilot plant.

- Pearson Technologies

Pearson Technologies is also discussed in this report in the Biomass Gasification above, in the context of being a biomass gasification process developer. Pearson Technologies has developed a 30-tpd biomass gasification and alcohols conversion facility in Aberdeen, MS. While both the gasifier and catalyst design are proprietary, it is believed that the catalyst is a modified F-T catalyst formulated to selectively increase the production of ethanol. The overall Pearson design includes alcohol fractionation and recycle, in an effort to purify the desired ethanol product.

A project is reported under development by the Worldwide Energy Group and the State of Hawaii to demonstrate gasification of sugarcane bagasse and production of ethanol using the Pearson technology on the island of Kauai. Funding for this project includes $50 million raised from special purpose revenue bonds issued by the state (Honolulu Star Bulletin, 2004). At the time of this report, it does not appear that a size or confirmed project timeline has been established.

3.3.3.5 Biomethanol

Overview

Today's methanol production technology employs a two-step process by first generating synthesis gas or syngas (carbon monoxide and hydrogen) from natural gas or other hydrocarbon feedstocks, such as naphtha, heavy oils, and coal. The syngas generated in the first step is then converted to methanol in the second step.

Biomethanol production process substitutes the feedstocks in the first step using various forms of biomass. The biomass feedstocks that have been used for biomethanol production include rice straw, husks of rice, sorghum, wood chips, sawdust, MSW, etc. The biomass feed is first dried and crushed before it is fed to the gasifier where gasification or partial oxidation takes place to produce raw syngas. The oxidant, typically 95 percent pure oxygen from an air separation unit, is preheated to minimize oxygen consumption.

The raw syngas exiting the gasifier is cooled before entering a gas purification unit and a syngas conditioning unit where the hydrogen to carbon monoxide ratio is adjusted to 2 to 1, as required by the methanol synthesis reaction. Methanol synthesis takes place in the synthesis reactor where raw methanol is produced. The raw methanol is then sent to distillation unit for purification.

It should be noted here that in addition to the biomass mentioned above, biomethane can also be used as feed. Biomethane typically contains a high concentration of carbon dioxide, resulting in low BTU characteristics of the bio-methane. Nexant has previously investigated the utilization of high CO_2 content natural gas and has concluded that with specially-designed methane reforming catalyst system, the high CO_2 content can benefit the syngas production process by eliminating the need for air separation, CO_2 removal, and syngas conditioning units. The ability to utilize CO_2 in feed gas, such as bio-methane, can provide higher carbon efficiency and reduce greenhouse gas emissions.

The details of biomass gasification are described elsewhere in this report and will not be repeated here. The following description pertains to methanol synthesis. Methanol synthesis technology is licensed by a number of companies, including One Synergy (an alliance formed by Johnson Matthey (JM) Catalysts, Davy Process Technology, and Aker Kvaerner), Lurgi, Haldor Topsoe, Mitsubishi Gas Chemical, etc. One Synergy has further chosen to license its process via one of seven sub-licensee contracting companies.

One Synergy Methanol Synthesis Technology

- Methanol Synthesis

The synthesis loop comprises a circulator, converter, feed/effluent exchanger, separator, and in some cases a heat recovery exchanger. The optimum operating pressure is typically about 80 bar for large plants, but for smaller plants (less than 600 ton/day) a pressure of 50 bar may be economical due to the reduced material requirements.

Synthesis gas is mixed with the recycle gas and preheated in a feed/effluent interchanger. The exact arrangement of interchanger is dependent on the type of converter used. The different types of converter offered by JM and its licensed contractors are detailed below.

The converter effluent is cooled by passing through the feed/effluent interchanger and dependent on the reactor type, a heat recovery exchanger. Prior to the catchpot, the gas is cooled to about 40°C to condense the product methanol. A purge is taken from the recycle gas to remove inerts (N_2, CH_4, Argon, and surplus hydrogen or carbon oxides) from the loop. This is used as fuel in the reformer. A purge gas expander may be used to recover power from the purge gas as it is let down to the fuel system pressure. Methanol recovery from the purge gas, by water wash, is a feature of modern designs.

With the JM Catalysts Low Pressure Methanol process a number of converter designs are available. The choice is influenced by feedstock composition, customer preference and plant size.

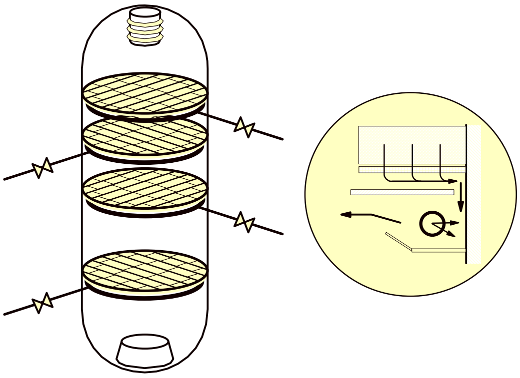
ARC Converter

Design

JM Catalysts, in conjunction with Methanol Casale, developed the ARC converter. This converter is based on the Quench type converter, in which the synthesis reaction is quenched by the addition of shots of cool synthesis gas between the beds. The quench is added to the gas reacting within the converter by means of banks of transverse sparger pipes which have a regular pattern of holes. The catalyst bed in a Quench converter is continuous.

The main feature of the ARC converter is that rather than having a single continuous bed of catalyst, each bed is discrete and is separated by plates. The shot is distributed within the converter by means of a torus, as shown in Figure 3.50.

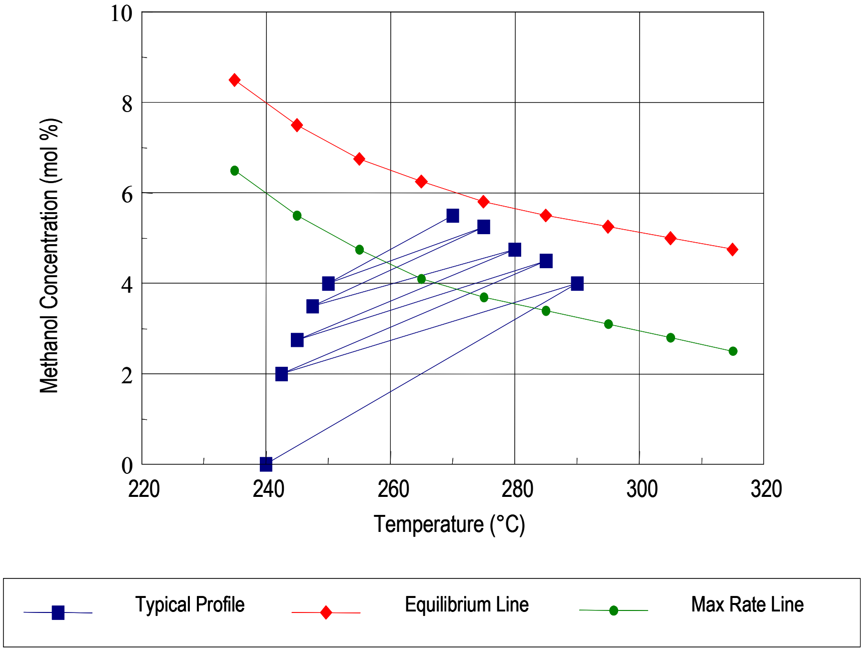
Figure 3.50 ARC Converter



Source: JM Catalysts

The converter temperature profile is shown in Figure 3.51.

Figure 3.51 Methanol Equilibrium Profile in Quench Converter



Source: JM Catalysts

Features

The ARC converter eliminates the propagation of maldistribution through the converter since each bed is separated and there is some cross mixing between beds. Typically, the mixing system can achieve a 1 or 2°C temperature spread inlet a bed with a spread of 5-10°C exit the previous bed.

This mixing system does increase the time for catalyst loading since the bed plates have to be fitted after each catalyst bed is loaded. Prior to catalyst discharge, the pyrophoric catalyst may be oxidized which increases shut down time by 2 to 3 days. As a retrofit, it can be installed in the converter within the time for a normal turn around. All components can be installed via a 24-inch manway and no welding is required.

Limited gas maldistribution within the converter allows the catalyst to be run close to the strike temperature and therefore much colder than an equivalent quench converter. This leads to higher catalyst activities, longer catalyst life and lower by-products.

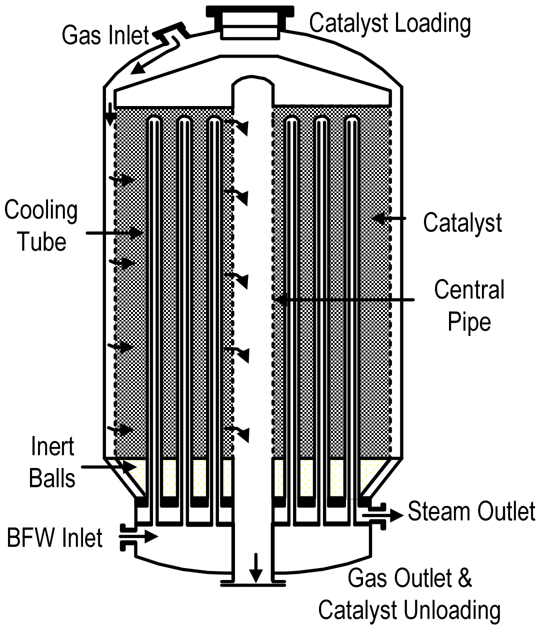
A single converter can produce in excess of 3 thousand metric tons per day. For 5 thousand metric tons per day, there is the option of two converters in parallel or to consider steam-raising options.

Toyo MRF – Z Converter

Design

The Toyo MRF-Z, as shown in Figure 3.52 is a unique converter in a number of respects. In this radial flow converter, steam is raised within a bayonet tube and effluent is collected in a central pipe.

Figure 3.52 Toyo MRF-Z Converter



Source: Toyo Engineering Corporation, 2006

Gas enters through the top of the converter and is distributed around the inside of the vessel wall by means of a scalloped distributor around the circumference of the vessel wall. The gas then passes through a continuous catalyst bed, which contains a number of rings of tubes. The tubes are fed with boiler feed water, which passes up through the center of the tube and then passes down through the outer bayonet tube and medium steam is formed by the absorption of the heat of reaction.

Features

The use of the bayonet tube avoids problems with thermal stresses and allows for free draining. Inspection of the tubes during maintenance is also easy as the inner tube can be withdrawn from the converter.

The benefit of a radial flow converter is that the pressure drop through the catalyst bed is low. The MRF converter can be scaled up to very large sizes (10 thousand metric tons per day) by extending the height.

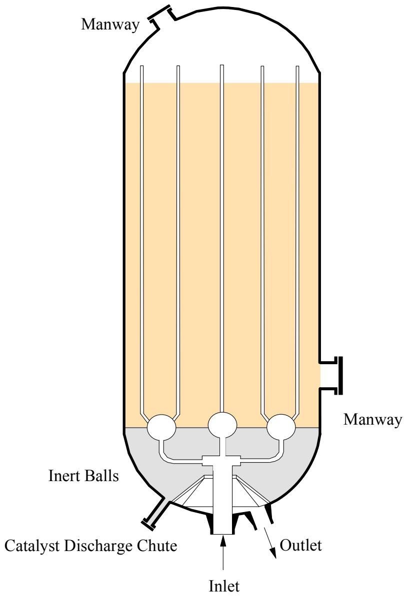
Natural circulation of the boiler feed water is not possible with the MRF-Z and so circulation pumps are required.

Tube Cooled Reactor

Design

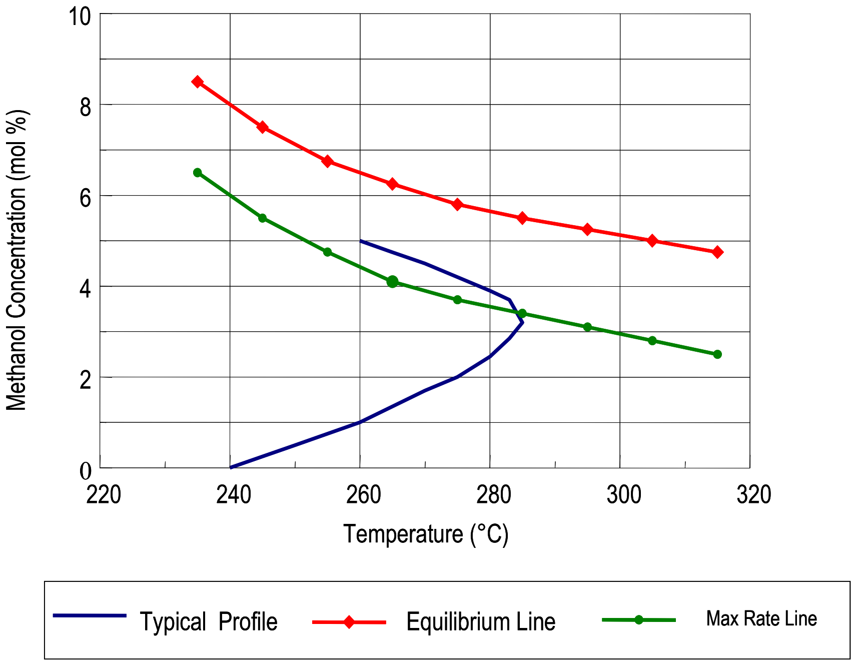
In JM Catalyst's tube cooled converter (TCC) design, circulating synthesis gas enters at the base of the reactor at around 140°C into the manifold system which distributes gas to the tubes of the internal heat exchanger. Synthesis gas is heated using the heat of reaction developed on the shell side of the converter as it passes up the tubes, reaching 240°C at the top. The gas then enters the catalyst bed and reaction commences. Figure 3.53 shows the schematic of the tube cooled reactor. The equilibrium profile in a tube cooled reactor is shown in Figure 3.54.

Figure 3.53 Tube Cooled Converter



Source: JM Catalyst, 2006

Figure 3.54 Methanol Equilibrium Profile in Tube Cooled Converter



Source: JM Catalyst, 2006

Mixing System

Some deficiencies in the basic TCC design result in hot and cold regions being apparent within the catalyst bed during operation. This leads to more rapid catalyst deactivation and high by-product levels, and will certainly lead to plant output being restricted before the catalyst has reached its design life. A TCC mixing system has been devised for new converters and for retrofits to overcome this problem.

Features

Tube Cooled Converters eliminate the need for a hot loop interchanger. As a result this type of loop is cheaper than an ARC loop at similar production rates.

As with the original quench converter, catalyst loading and discharge are easy because the bed is continuous. TCC are very simple to operate since only the turn temperature has to be controlled.

A single reactor can produce two thousand metric tons per day.

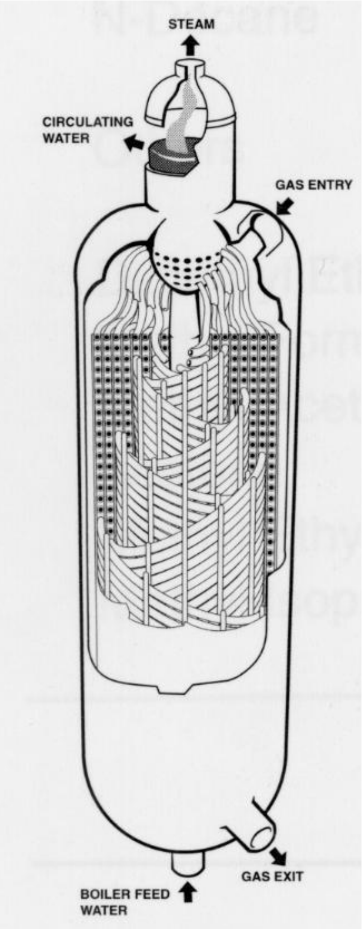
The Linde Steam Raising Converter

Design

Linde, a licensed contractor for JM Catalysts, has developed their own steam raising converter that they call the Isothermal reactor. The catalyst bed, which is on the shellside, surrounds a spiral wound heat exchanger through which passes boiler feed water. The heat of reaction is used to raise steam at between 25 and 35 bar. Boiling water enters the tubes at the base of the converter and circulates through natural draft while the steam is collected in a steam drum which is an integral part of the converter. The schematic of the Linde stream raising converter is shown in Figure 3.55.

The catalyst is enclosed in a steel sheath, which is welded to the bottom of the vessel. This sheath prevents the reacting gas from bypassing the tubes.

Figure 3.55 Linde Stream Raising Converter



Source: Linde

Features

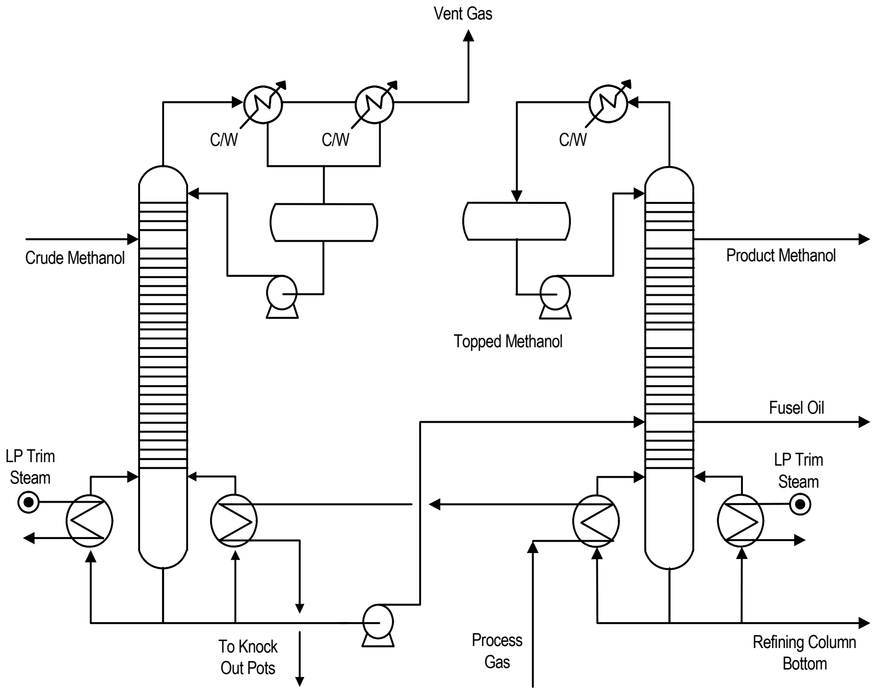
Since the catalyst bed is continuous and there is sufficient distance between the tubes, discharge of the catalyst is easy. The maximum plant size that could be achieved with a single such converter is over 2 thousand metric tons per day.

As with all steam raising converters, by-product formation is low as the operating temperatures are low.

Distillation

The crude methanol from the separator contains both water and low levels of by-products, which must be removed to achieve required product purity. JM Catalysts offers both two and three column designs as shown in Figure 3.56, which can easily achieve US Federal AA grade purity product. The US Federal AA grade specification is the most commonly accepted specification in world methanol trade.

Figure 3.56 JM Catalyst Methanol Distillation System



Source: JM Catalyst, 2006

Uhde Methanol Synthesis Technology

The methanol synthesis operates typically at a pressure range between 90-100 bar. As one of the limited licensees of Johnson Matthey Catalysts, Uhde offers nearly every methanol reactor type commercially available, e.g., quench (ARC) converter, steam raising converter (straight tube or helical coil), or tube cooled converter.

A serial converter design achieves a higher methanol outlet concentration compared to parallel converter arrangements, allowing the methanol synthesis loop to operate at very low recycle ratios down to 2.0. This leads to lower equipment costs and a lower recycle power requirement in the synthesis section. However, a serial arrangement reduces the overall carbon efficiency of the methanol loop.

On the other hand, a parallel converter design leads to an increased recycle flow rate resulting in higher loop investment costs. However, it provides an advantage of increased methanol production rate at a fixed make-up gas flow rate compared to a serial design. An increased recycle rate also lowers the by-product formation due to the reduced reactivity of the methanol converter feed stream.

Therefore, the optimum solution is determined by the actual requirements and boundary conditions as specified by the client.

Lurgi Methanol Synthesis Technology

Lurgi methanol synthesis is based on its Combined Converter Synthesis, which has been developed and patented to improve the overall economics. In the first stage, the synthesis gas is partly converted to methanol in a conventional water-cooled steam generating Lurgi reactor. This reactor operates at very high yield and at higher than normal reaction temperature allowing higher pressure steam to be produced, which improves the energy efficiency of the plant.

In the second converter, the reaction rate is much lower and, consequently, so are the space time yield and the amount and grade of the reaction heat. The remaining reaction heat is used to preheat the feed gas to the first converter. The continuously reduced temperature in this reactor provides increasing thermodynamic equilibrium potential. Since the temperature difference between the reaction and the cooling gases is higher than in a conventional inlet/outlet heat exchange, the required heat exchange surface is relatively small, which allows a large catalyst volume at a moderate vessel size.

The operating and design parameters for the methanol converter are presented in Table 3.25.

Table 3.25 Operating and Design Parameters for Methanol Converter of Lurgi Mega Methanol Process

Stoichiometric number of reformed gas, SN = $(H_2-CO_2)/(CO+CO_2)$	1.81	
Hydrogen recycle	1,750	kmol/hr
Syngas flow(1)	19,000	m^3/hr
Stoichiometric number of syngas, SN = $(H_2-CO_2)/(CO+CO_2)$	2.06	
Syngas compressor suction pressure	32	bar
Syngas compressor discharge pressure	71	bar
Recycle ratio	1.9	
Methanol content in reactor exit gas	11.5	mol%

(1) At suction syngas compressor

Source: Lurgi

High pressure steam is generated from process heat in the reforming section and is used for the major steam turbine drives. Medium pressure steam is generated in the steam drum of the first methanol reaction stage and mainly used as process steam.

The advantages offered by Lurgi's Combined Converter Synthesis include:

- High synthesis gas conversion efficiency
- Extended catalyst life
- High energy efficiency
- Drastically reduced loop size
- Large single train capacity
- Low investment cost

Finally, the crude methanol produced in the converters is routed to the distillation system to produce Federal Grade AA methanol. A three-column design is employed. This design allows a single train distillation for the desired capacity.

3.3.4 Derivatives

3.3.4.1 *Ethanol to Ethylene*

Chemistry

The use of ethanol to make ethylene on a comparatively small scale has been well demonstrated in Brazil and India at a time when they did not have ready access to hydrocarbons. The chemistry of ethylene production via dehydration of ethanol can be represented by the following reaction:

$$CH_3CH_2OH \longrightarrow CH_2{=}CH_2 + H_2O$$

The dehydration reaction is carried out at 315-425°C (599-797°F) over specially treated activated alumina catalyst. The ethylene is obtained in high purity in yields of approximately 96 percent. A conventional purification scheme may be used to remove any trace by-products.

The reaction is endothermic requiring about 390 kcal per kg of ethylene produced. In addition, the reaction is reversible with the equilibrium being favored by high temperatures and hindered by higher pressures and the presence of water vapor in the feed. The recovery of unconverted ethanol for recycling is energy and capital intensive and reaction conditions enabling greater than 99 percent conversion of ethanol are usually preferred.

The conversion of ethanol is highly selective with the reaction products containing essentially only ethylene and water. Minor other constituents are methane, carbon oxides, ethane, propylene, butanes acetaldehydes, diethyl ether, hydrogen, and any unconverted ethanol.

Process Description

Ethanol can be converted to ethylene in either a fixed-bed or fluid-bed reactor. The fixed-bed route is licensed by Chematur Engineering AB and is presented herein. Processing of the reactor effluent to product ethylene is quite simple. It is first cooled to allow most of the water to condense. The resulting gas steam is compressed, cleaned in a water scrubber to remove oxygenated impurities, cooled to remove condensables, and finally dried in a molecular sieve bed to remove residual water. A process diagram for Chematur's fixed-bed, ethanol-based ethylene plant is illustrated in Figure 3.57.

The ethanol feed is supplied from an offsite storage tank to the vaporizer. The vaporized ethanol is then heated to the reaction temperature in the preheat section of the furnaces and then passed to the first of the four adiabatically operated catalyst beds in the reactor. Ethanol is converted to ethylene as it passes over the catalyst and because of the endothermic reaction; the reaction gases cool progressively thereby lowering the reaction rate. The effluent gases from the first bed are therefore heated in the furnace again to the desired temperature and then sent to the second bed of the reactor where some more ethanol is converted. Similar operations are conducted in the third and fourth beds of the reactor. The dehydration reaction, carried out at 315°C to 42°C (599°F to 797°F), is an endothermic reaction. Temperature is a critical operating parameter: excessive temperatures produce aldehydes and low temperatures produce ether. The reactor design must therefore evenly distribute the heat input to eliminate hot and cold spots. Coke does not have to be removed from the SD catalyst (SynDol) in the Chematur process. The catalyst is stable for at least two years.

The hot ethylene-water vapor mixture leaving the last bed of the reactor enters the waste heat boiler where some of the heat is recovered as steam. The cooled gases, comprising mainly ethylene and reaction product water, are quenched by direct contact with water in the quench system, which also dissolves any unreacted ethanol and some by-product impurities (e.g., aldehyde and ether). In this system, the ethylene is cooled and separated from the unreacted ethanol and some of the by-products. The quench water is recirculated for heat removal and wastewater is purged.

Upon leaving the top of the quench system, the ethylene is compressed and passed in series through a caustic scrubber and a fixed bed gas dryer to reduce the concentrations of oxygenated impurities and water to specification levels.

The ethylene from the dryer is distilled in an ethylene column operating at low temperature where heavy impurities are removed. The ethylene product from the overhead of this column meets all polymer grade (99.95 minimum volume percent) specifications except for carbon monoxide.

To reduce the carbon monoxide to specification levels, the overhead to the ethylene column is sent to a stripper where the carbon monoxide is stripped from the ethylene. The overheads from the ethylene column and stripper use a common condenser and accumulator. The carbon monoxide is purged from the accumulator with a small loss in ethylene. Product ethylene recovered from the bottom of the stripper is used to cool a number of process streams and is then delivered to the battery limits as a vapor.

Lummus has developed a catalyst and process for the dehydration of ethanol to ethylene utilizing fluidized-bed technology. The fluidized-bed reactor affords highly efficient temperature control, high rates of heat and mass transfer, uniform catalyst activity, continuity of operation and the ability to process large quantities of reactants with minimum mechanical devices and operating labor. The required heat of reaction is supplied by circulating fluidized catalyst from the regenerator. Because of the highly agitated state within the fluidized catalyst bed, there are no localized hot or cold spots, and a virtually uniform temperature exists throughout. While a 75 million pound per year ethylene plant requires three fixed-bed reactors with their auxiliary equipment, it is claimed that this output (and outputs up to 220 million pounds per year) can be produced from a single fluidized-bed reactor. In large plants, the fluidized-bed reactor system may thus be much more economic than the fixed-bed system. The flowsheet downstream of the reactor is similar to that for the fixed-bed process. The fluidized-bed process is illustrated in Figure 3.58.

Figure 3.57 Ethylene from Ethanol (Chematur Route)

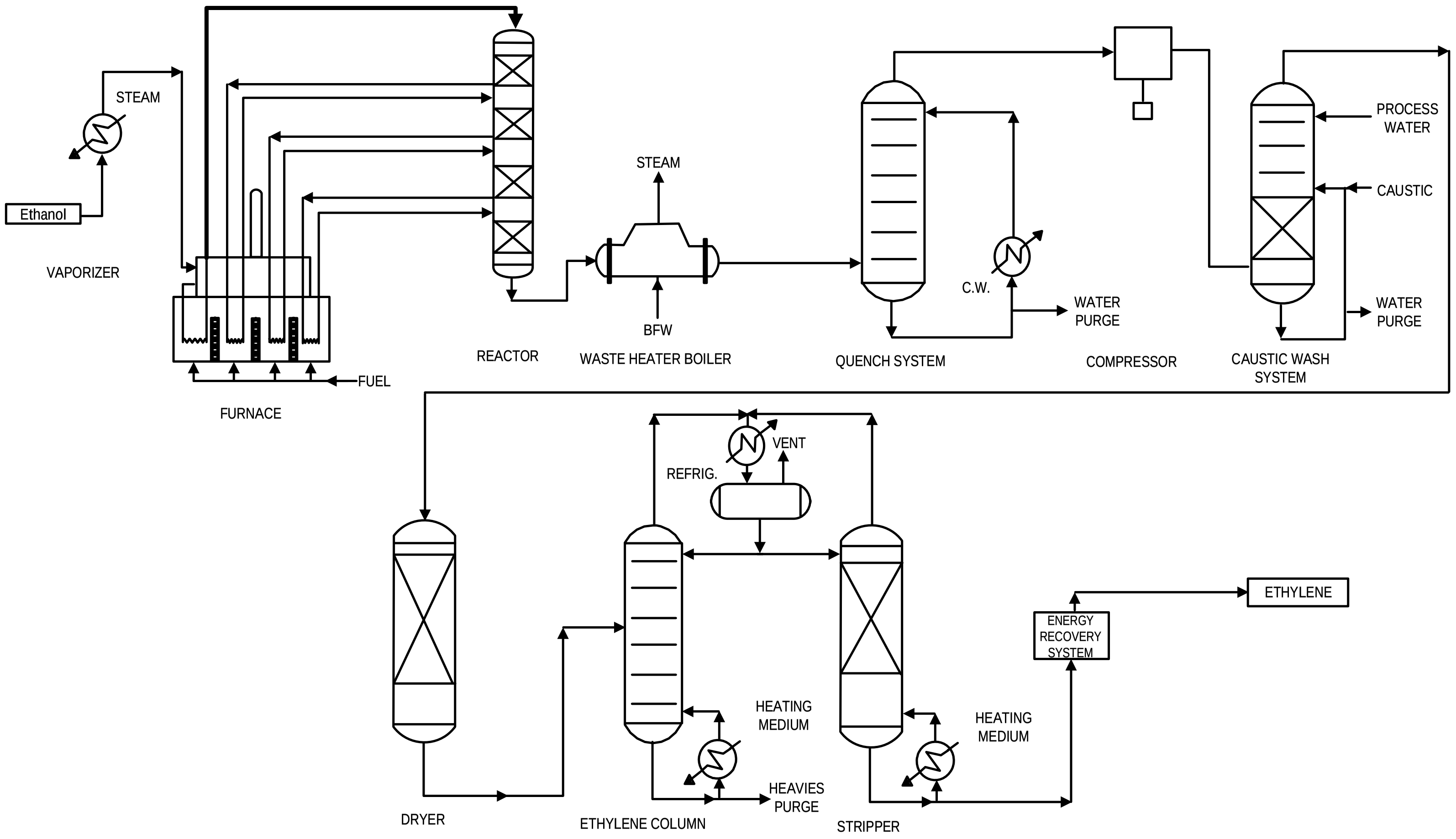
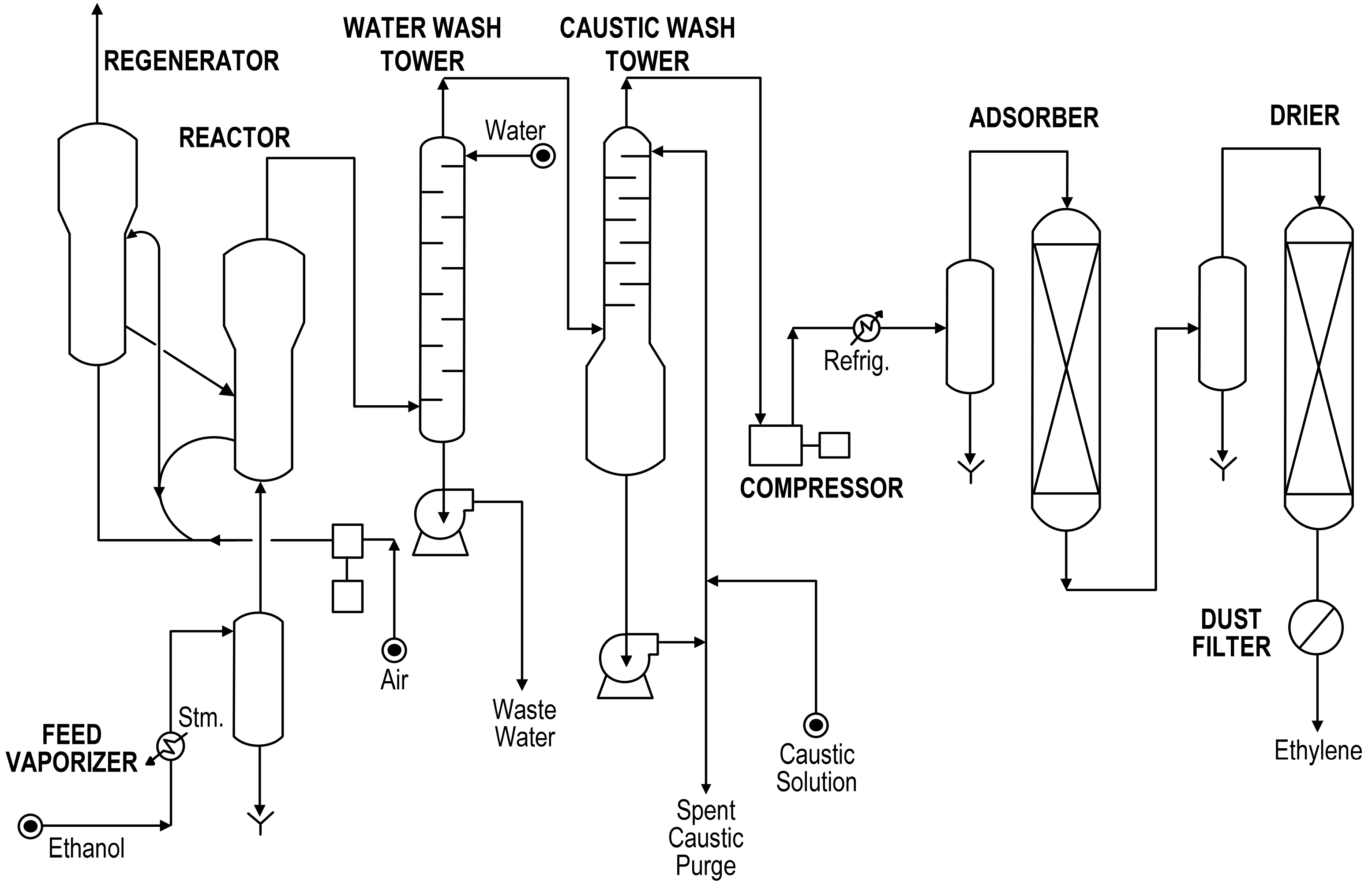


Figure 3.58 Ethylene from Ethanol – Lummus Fluid Bed Process



3.3.4.2 MTG/ETG

Methanol-to-Gasoline (MTG)

The original MTG (methanol-to-gasoline) technology was developed in the 1970s-1980s by ExxonMobil based on natural gas. It was commercialized in New Zealand in 1985 and produced approximately 14,500 barrels per day of gasoline for over 10 years. The MTG technology is a catalytic process which converts methanol to liquid transportation fuel, such as gasoline.

The MTG technology has been improved over the years. The sources of methanol for the process are syngas, either based on natural gas reforming or coal gasification. Other sources for methanol can be either petcoke or biomass. The coal to methanol to gasoline conversion gives way to another route known as the Fischer-Tropsch (F-T) method which converts coal to liquid fuel. The difference between the F-T approach and the MTG process is that the F-T method is usually utilized for the production of diesel fuel or lubricants while the MTG process is mainly used for the production of premium gasoline.

In the MTG process, the conversion of methanol to hydrocarbons and water goes to almost completion and is in essence stoichiometric. The overall reaction is exothermic where the conversion is split into two parts to manage the heat resonating from the reaction. The first part is where the methanol is converted to an equilibrium mixture of methanol, dimethylether (DME) and water. The equilibrium mixture is then mixed with recycle gas and is passed over a shape selective catalyst, a ZSM-5 zeolite catalyst, to form hydrocarbons and water. The product gasoline generated from the process is a premium quality clean gasoline which can be blended with refinery gasoline directly or it can be sold separately.

The gasoline product from the MTG process has advantages over the fossil fuel based counterparts. The ExxonMobil product is an ultra clean, high-octane gasoline which is compatible with the refinery product of regular gasoline. It has a low sulfur, benzene, and nitrogen content. The MTG process has a simple and reliable adiabatic fixed bed reactor design and is economically competitive with other alternative ways of making high-octane gasoline.

Figure 3.59 displays the overall process of producing the gasoline from the MTG technology.

Typical MTG gasoline product quality is shown in Table 3.26, including the composition volume percent of the components and specific gravity of the product.

Table 3.26 Typical MTG Gasoline Product Quality

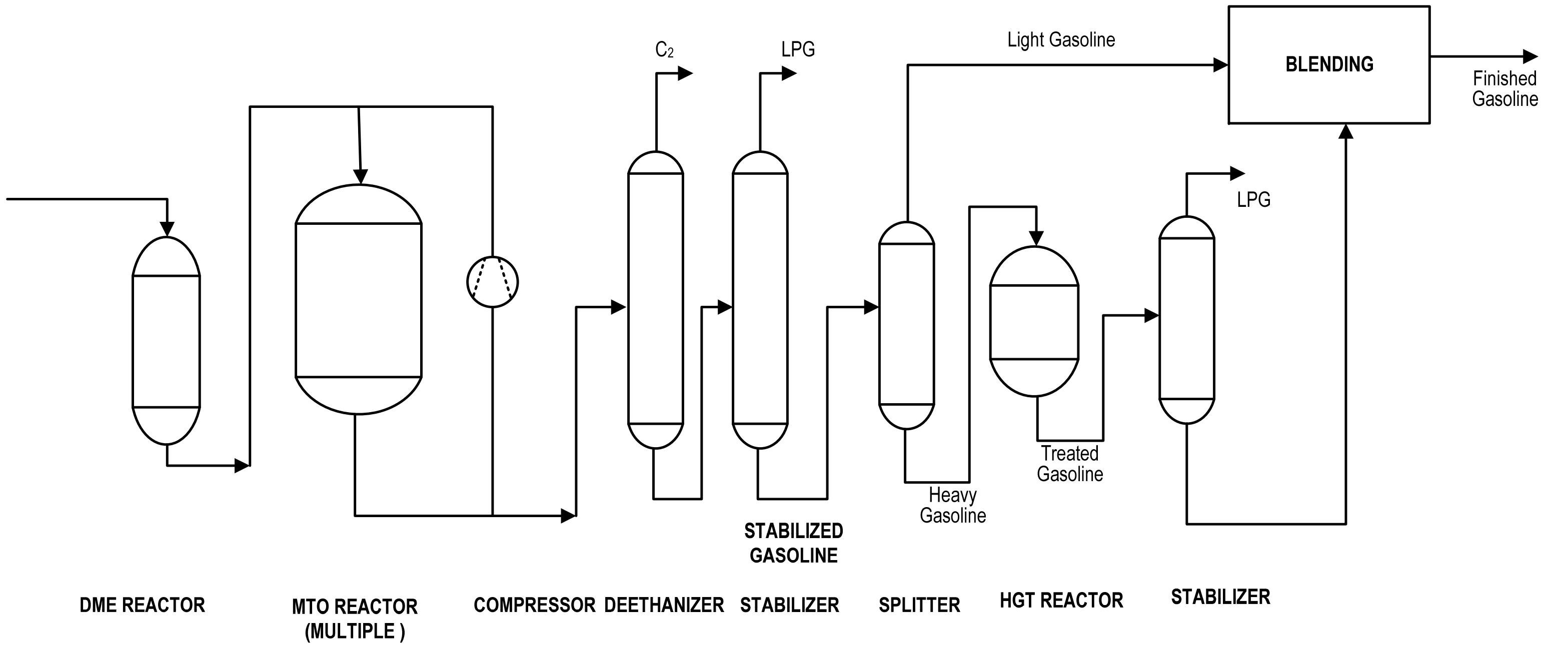
Octane, RON	92
Octane, MON	82
RVP, kPa	62
Specific Gravity	0.732
Composition (Vol %)	
Paraffins	52.4
Olefins	12.6
Naphthenes	8.5
Aromatics	26.5
Benzene	0.3
ASTM D-86 Distillation (°C)	
IBP	51
10%	55
50%	94
90%	160
FBP	180

Source: ExxonMobil

Ethanol-to-Gasoline (ETG)

Mobil's ETG (ethanol-to-gasoline) process was developed in the 1970s-1980s, but there are no recent references to it. At the time it was developing ETG, Mobil estimated costs of $1.58-$1.67 per gallon of gasoline produced from ethanol priced at $1.00/gallon. The process was to use a relatively inexpensive zeolite ZSM-5 catalyst in a circulating fluid bed reaction configuration. In the ETG process, ethanol undergoes dehydration, followed by a shape-selective transformation to hydrocarbons.

Figure 3.59 ExxonMobil MTG Process Flow Diagram



Mobil identified many opportunities for thermally integrating the exothermic dehydration of ethanol to gasoline with the endothermic production of ethanol from corn. Much of their thinking was leveraged on their greater experience with MTG (methanol-to-gasoline) gained from their pilot plant and designs of semi-commercial facilities in New Zealand based on reforming natural gas feedstock and synthesizing methanol as a feedstock for MTG. Compared to methanol, which theoretically "contains 44 percent hydrocarbons", net of the oxygen atom contained in the alcohol molecule, ethanol contains 61 percent hydrocarbons net of its oxygen content. Table 3.28 displays the comparison of the composition of hydrocarbon components for methanol and ethanol feedstocks.

The ETG process, it was claimed by Mobil, could run on ethanol that has not been dehydrated, such as azeotropic, hydrous ethanol, 80-proof rum, and even crude "beer" from fermentation. These grades of ethanol could be handled, however, with increasing processing costs in this order, in a trade-off against the transfer price of the feed in an integrated facility.

Typical weight percent compositional yield is shown in Table 3.27, including both gasoline (C_4-plus) and lights (C_4-minus).

Table 3.27 Typical ETG Composition

Propane	12.17
Iso-Butane	10.25
Iso-Pentane	9.39
Iso-Hexanes	5.62
Toluene	6.95
Xylenes	9.56
Trimethyl benzenes	3.7
Methyl-ethyl benzenes	4.37
Other C_{10} benzenes	3.27
Others	34.72
Total C_4+ gasoline	85.61

Source: ExxonMobil

Table 3.28 Composition of Hydrocarbon Components for Methanol and Ethanol Feedstocks
(Weight Percent of Hydrocarbons)

Feedstock	Methanol	Ethanol
Methane	1.14	0.28
Ethane	0.50	1.78
Ethene	0.03	0.01
Propane	5.70	12.17
Propene	0.22	0.15
n-Butane	3.24	7.75
i-Butane	8.69	10.25
Butenes	1.08	0.68
n-Pentane	1.63	3.77
i-Pentane	11.13	9.39
Pentenes	2.09	0.77
Cyclopentane	0.33	0.35
Methylcyclopentane	1.57	1.09
n-Hexane	0.83	1.15
Methylhexanes	4.61	1.77
i-Hexanes	11.72	5.62
Hexenes	1.49	0.38
n-Heptane	0.21	0.22
i-Heptanes	0.50	0.45
C_7-Olefins	1.91	0.45
Dimethyl-N5	1.82	1.14
n-Octane	0.04	0.00
i-C_8-P + O + N_5 + N_6	6.73	3.01
n-Nonane	0.14	0.07
i-C_9-P + O + N_5 + N_6	2.43	0.86
n-Decane	0.00	0.00
i-C_{10}-P + O + N_5 + N_6	0.77	0.17
Unknowns (hydrocarbon aromatics)	0.11	0.30
Benzene	0.23	0.93
Toluene	2.22	6.95
Ethylbenzene	0.64	2.00
(p+m)-Xylenes	6.95	7.44
o-Xylene	1.90	2.12
Trimethylbenzene	6.66	3.70
Methyl-ethyl-benzenes	2.74	4.37
C_3-Benzenes	0.15	0.24
1,2,4,5-Tetramethylbenzene	3.71	0.16
1,2,3,5-Tetramethylbenzene	0.24	0.11
1,2,3,4-Tetramethylbenzene	0.11	0.29
Other C-_{10} benzenes	1.65	3.27
C_{11}-Alkylbenzenes	0.54	1.53
Naphthalenes	0.07	0.35
Unknowns (all other)	1.33	2.52
(Total C_4 + gasoline)	92.41	85.61

Source: Chemtech, August 1983

3.3.4.3 Guerbet Reaction – Ethanol Condensation to Butanol

Synthesis of higher alcohol from lower alcohol is generally known as the Guerbet reaction, for which solid-base catalysts or supported metal catalysts can be used. The synthesis of *n*-butanol from ethanol is believed to be indirect process via acetaldehyde. However, the possibility of direct synthesis of *n*-butanol from ethanol over a multicomponent oxide catalyst (MgO-CuO-MnO), alkali cation zeolites, or a MgO catalyst has also been suggested.

Although the elementary reactions of this synthesis have not been clarified, the process involves dehydration of two molecules of ethanol in the overall chemical reaction formula:

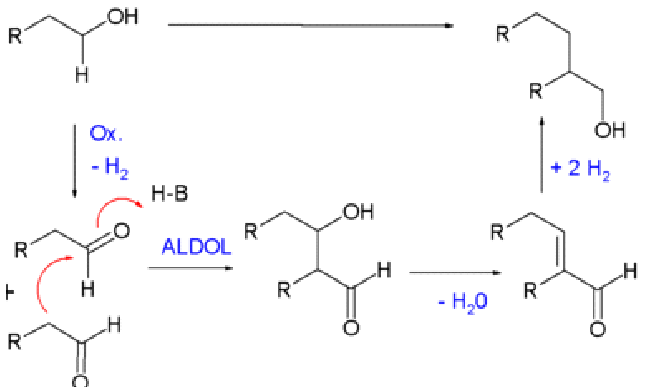
$$2C_2H_5OH \longleftrightarrow C_4H_9OH + H_2O$$

The Guerbet reaction converts primary aliphatic alcohols into their beta-alkylated dimer alcohols, known as "Guerbet alcohols", which yields also a mole equivalent of water. The reaction operates with a catalyst and at elevated temperatures.

The reaction occurs in four sequential steps:

- Oxidation of alcohol to aldehydes
- Aldol condensation after proton extraction
- Dehydration of the aldol product
- Hydrogenation of the allylic aldehydes

This sequence can be depicted as follows:



The sequence has the following known characteristics:

- Can occur without catalysis, but it is strongly catalyzed by hydrogen transfer catalysts
- At low temperatures of 130-40°C, the oxidation process (e.g., hydrogenation of the aldehyde) is the rate-limiting step
- At somewhat higher temperatures of 160-80°C, the aldol condensation is rate-limiting
- At yet higher temperatures, other degradation reactions occur and can dominate

The reaction requires catalysts such as alkali metal hydroxides or alkoxides and hydrogenation catalysts such as Raney Nickel at higher temperature (220°C) and pressure. Many catalysts have been described in the literature as effective for the preparation of Guerbet alcohols. These include, nickel, lead salts (US Patent 3,119,880), oxides of copper, lead, zinc, chromium, molybdenum, tungsten, and manganese (US Patent 3,558,716). Later US patents (US Patent 3,979,466) include palladium compounds and silver compounds (US Patent 3,864,407). Each type has advantages and disadvantages.

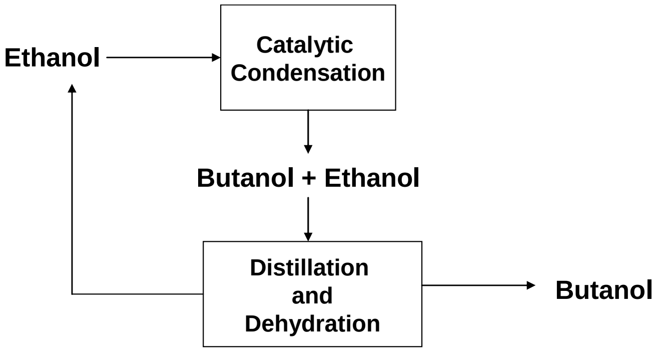
The Guerbet reaction competes with the Cannizzaro reaction whereby two aldehyde molecules disproportionate to form the corresponding alcohol and carboxylic acid. Another side reaction is the Tishchenko reaction.

The original 1899 publication of the reaction treated a reaction of significant economic interest, production of 2-ethyl-1-hexanol (2-EH) from *n*-butanol. In fact, much of the historical and current literature involves this condensation. The long-chain aliphatic alcohols produced are commonly used to manufacture surfactants.

Reacting ethanol with methanol yields a mixture of propanol, isobutanol, and 2-methyl-1-butanol. These higher alcohols are all useful as solvents, chemical intermediates, and fuel additives with higher market values than ethanol and methanol.

The important consideration for this report is that *n*-butanol (biobutanol) can be made by the self-condensation of bioethanol in the multi-step Guerbet reaction occurring on a single catalytic bed. This is shown in the schematic of Figure 3.60.

Figure 3.60 Schematic of Guerbet Ethanol Condensation



3.3.4.4 *Sangi Catalyst – Ethanol to Gasoline*

Sangi Co., Ltd. (Japan) has developed a series of processes for ethanol dehydration to *n*-butanol, biogasoline, or hydrocarbons. This technology development is based on their core competency with hydroxyapatite (HAP), which is used as a ceramic material in dentistry and other health care industry applications. HAP is a “distorted” apatite, which is expected to have high catalyst activity, with acidity controlled by changing Ca/P mole ratio between 1.50-.70.

In discussions with Sangi, it was learned that they have explored synthesis of n-butanol, $C_4/C_6/C_8$ alcohol mixtures, 1,3-butadiene, and “biogasoline” (e.g., 4+ mixtures that appear to be attractive high-octane blendstocks for petroleum-derived gasoline). Sangi has evaluated HAP catalyst in laboratory in a 20 liter reactor with ethanol feed rate of 52 ml/min, 0.6 ml of catalyst, at 1 atm, achieving the conversions of ethanol to *n*-butanol, other chemicals, or gasoline (as of 11/8/2004) as shown in Table 3.29.

Table 3.29 Sangi HAP Synthesis Exploratory Results

Product	Reaction Temp, °C	Conversion, %	Selectivity,%	Yield, %
1-Butanol	300	14.7	77.9	11.5
C_4/C_6/C_8 Alcohol	300	14.7	87.7	12.9
1,3-Butadiene	425	89	28.6	25.4
Biogasoline (C_4+)	425	99.4	88.8	88.3

Source: Sangi Co., Ltd, 2006

Reactivity increases with temperature (accelerated above 400°C) but is little affected by pressure. HAP catalyst is inexpensive to begin with, and can be regenerated by heating and completely reactivated.

Sangi's patent, "Synthesis Method of Chemical Raw Materials and Fuel Oil", has been applied for internationally (PCT/JP99/00347), and is registered individually in the US (6323383-US), Canada (2,319,006-CA), Australia (748108-AU), China, Russia, and Korea.

Catalyst development started in 1996, jointly with Kyoto University (over two years). Since 2004, Sangi collaborated with Hokkaido University. In 2005, Sangi applied to NEDO (New Energy and Industrial Development) for a joint grant with Hokkaido University, the Industrial Research Institute and a chemical company. The grant is for 100 million yen per year (about $1 million per year) for three years. This is expected to establish the HAP technology in two steps:

Step 1: Clarify catalyst mechanism, improve catalyst reactivity, scale up to pilot plant, and establish production technology and design.

Step 2: Make catalyst available for the pilot plant, reduce catalyst cost optimize specification, design and operate a pilot plant, optimize process, and confirm process viability.

Sangi HAP Biogasoline ex. Ethanol

Biogasoline synthesis requires the most severe conditions (475°C reaction) among these products, but gives the highest conversion, selectivity, and yield (99.4 percent - 88.8 percent, and 88.3 percent, respectively). Sangi projects competitive economics for biogasoline

Making biogasoline at a dry corn mill with this process may allow the mill to make "gasohol" mixtures (e.g., E85) completely independent of any petroleum source (and that are 100 percent renewable). Again, E85 is required because neat ethanol has insufficient vapor pressure to allow cold starts and some gasoline is needed to assist ignition. In very warm climates, this is not an issue, and net anhydrous or hydrous (azeotropic) ethanol can be used in vehicles with gasoline added as an ignition "pilot" material (also serving as a denaturant).

A sample product of gasoline from ethanol via Sangi HAP as analyzed by Nippon Oil seems to be a feasible blendstock for petroleum-derived gasoline, as indicated in Table 3.30.

Table 3.30 Comparison of Sangi HAP Properties with Typical Petroleum Gasoline

	Sangi HAP Gasoline	Typical Gasoline
Density - kg/m³	805.1	715 - 770
Octane value (RON)	96.1	92-95
Vapor Pressure (kPa)	35.5(1)	45-60
Initial Boiling Point °C	47.5	25 Min.
Fractional Boiling Pts. (°C)		
30 Vol. %	79	T10 = 55-70
50 Vol. %	106	77-110
80 Vol. %	142	--
95 Vol. %	180.5	T90 = 130-190
End Point	214	210-215
Residue Vol. %	1	2 Max.
Oxidation Stability	Min. <1,440	480 Min.
Total Heat Generation	39,260 J/g	5.253 MM Btu/bbl

(1) Generally lower vapor pressure is better, allowing refiners to blend with high pressure material

Source: Nippon Oil Laboratory

3.3.5 Hydrocracking FOGs

3.3.5.1 NExBTL – Neste Oil

Neste Oil Corporation is a leading Finnish oil refining and marketing company, with refineries located in Porvoo and Naantali, Finland, and a total refining capacity of about 250 thousand barrels per day. Neste has also signed a Memorandum of Understanding (MoU) with French major oil company Total to evaluate jointly building a large-scale NExBTL plant adjacent to one of Total’s oil refineries, with the aim of beginning production in 2008. Neste Oil has also established a marketing office in Houston, Texas, and has stated intentions to use this venue as a platform for other joint ventures in the United States.

Neste Oil’s NExBTL biodiesel technology (which stands for “Next Generation Biomass to Liquid”) is based partly on patents, but also on much unpatented know-how, according to the developers. Therefore, Neste Oil is maintaining a relatively closed stance on information-sharing. The NExBTL process was originally developed when Neste Oil was part of Fortum several years ago, under whose name some of the patents on this technology were filed. Apart from feedstock flexibility, NExBTL includes excellent fuel properties that meet the highest requirements of automotive industry, as well as remarkably low exhaust emission levels. The first NExBTL plant is due to come on-stream in summer 2007 at Neste Oil's Porvoo refinery with a capacity of 170 thousand tons per year. The NExBTL technology produces synthetic biofuels as defined by the Directive 2003/30/EC on biofuels development in the European Union. As with other biofuels already available in the market, the NExBTL products should benefit from the tax relief aimed at encouraging the production of biofuels.

Neste Oil claims that the NExBTL process can feed a broad variety of natural oils and fats, from fish oils and tallow to soybean and rapeseed oils. The first generation of NExBTL is available commercially and the second generation is available technically. The second generation technology expands the raw material window to the use of any fatty acid, and perhaps even more highly oxygenated and unstable pyrolysis-derived bio-oils in the future. The fats are not transesterified, but are catalytically hydrotreated (hydrogenated), and following this, hydrogenate is isomerized. The product is more stable, independent in properties from the type of feedstock used, and compatible with petroleum diesel than are methyl ester biodiesel products. Cetane numbers are very high, and NOx and PM emissions are extremely low compared to ultra low sulfur diesel, any methyl ester biodiesel, and GTL (natural gas-derived Fischer-Tropsch synthesized liquid hydrocarbons). NExBTL product has no unsaturated components and therefore stability is excellent. It is free from aromatics and the lubricity requirements can be fulfilled with the additives normally used for sulfur-free diesel fuel. NExBTL behaves like non-aromatic hydrocarbons for materials of construction in the fuel system, so there are no new requirements for gaskets etc. in this respect. As such, NExBTL easily meets Ultra Low Sulfur Diesel requirements.

NExBTL fuel has other property advantages:

- Fits into existing infrastructure without incremental costs
- No storage stability problems
- Excellent performance in cold climates
- Very high cetane number (84 - 99)
- Free of aromatics, sulfur, oxygen
- Reduces NOx, PM, HC & CO exhaust emissions

Neste Oil has provided the fuel property comparison between NExBTL and other diesel fuels shown in Table 3.31.

Table 3.31 Biodiesel Fuel Property Comparison

	NExBTL	GTL	FAME (RME)	Sulfur Free Diesel Fuel *(summer)*
Density at +15 °C (kg/m^3)	775…785	770…785	≈885	≈835
Viscosity at +40 °C (mm^2/s)	2.9…3.5	3.2…4.5	≈4.5	≈3.5
Cetane number	≈84…99*	≈73…81	≈51	≈53**
Cloud point (°C)	≈-5…-30	≈0…-25	≈-5	≈-5
Heating value (lower) (MJ/kg)	≈44	≈43	≈38	≈43
Heating value (MJ/l)	≈34	≈34	≈34	≈36
Polyaromatic content (wt. %)	0	0	0	≈4
Oxygen content (wt. %)	0	0	≈11	0
Sulfur content (mg/kg)	<10 (<1)	<10	<10	<10
Carbon/Hydrogen	≈5.6	≈5.6		≈6.0

* Blending Cetane number

** ASTM specification > 40

A specific feature claimed by Neste Oil for the NExBTL process is the flexibility to produce diesel oil with cloud points optimized according to requirements. Except for density, which is below the standard level for conventional diesel, pure NExBTL product meets EU blending requirements. Only its light density limits blending it up to about 65 percent volume in petroleum diesel, which does not present a practical restriction for refinery operations. Its hydrocarbon molecular structure makes the mutual solubilities of NExBTL and water very low.

Rather than making a by-product of glycerol, the process makes propane. However, Neste Oil has provided only limited information on catalysts employed and on factors that Nexant would normally consider in a cost of production analysis as presented herein.

Propane production absorbs about 70 percent of the gross hydrogen fed to the hydrogenation, but this propane can optionally either go to the refinery's gas recovery section, to petrochemical production, LPG fuel blending (e.g., for bio-fueled fork lifts, cooking, remote heating applications, fuel cells, etc.), or can be recycled to a reformer for more hydrogen production. Total absorbed hydrogen is 2 percent by weight in the product, 3-4 percent of gross feed. The actual hydrogen source currently at Porvoo is reformer hydrogen, so that the product ends up being about 4 percent non-biomass based. However, in the future, conventional reforming with bio-methane net feed and recycled propane could be the hydrogen source for a 100 percent bio-based product.

Actually, yields on feed by weight are:

- 84 percent NExBTL biodiesel liquid fuel (largely independent of feedstock type)
- 2.5 percent biogasoline (lower boiling point than diesel), which can be blended in the gasoline pool or with NExBTL, since it is mostly low octane linear alkanes
- 11 percent fuel gas, which is 70 percent propane. Neste Oil is open to either licensing or joint venture development for NExBTL technology

Neste Oil gave combined catalyst and utility costs of production of around € 23 per biodiesel ton, and capex for Porvoo's 170 thousand tons per year capacity as € 50 million installed ISBL, and less than € 100 million total capex.

Neste Oil has built an 800 thousand ton per year renewable diesel plant in Singapore based on its NExBTL technology. It is the largest facility worldwide for producing diesel from renewable sources. The new plant in Singapore will provide this APEC member economy an opportunity to develop into a center for Asian biofuel production.

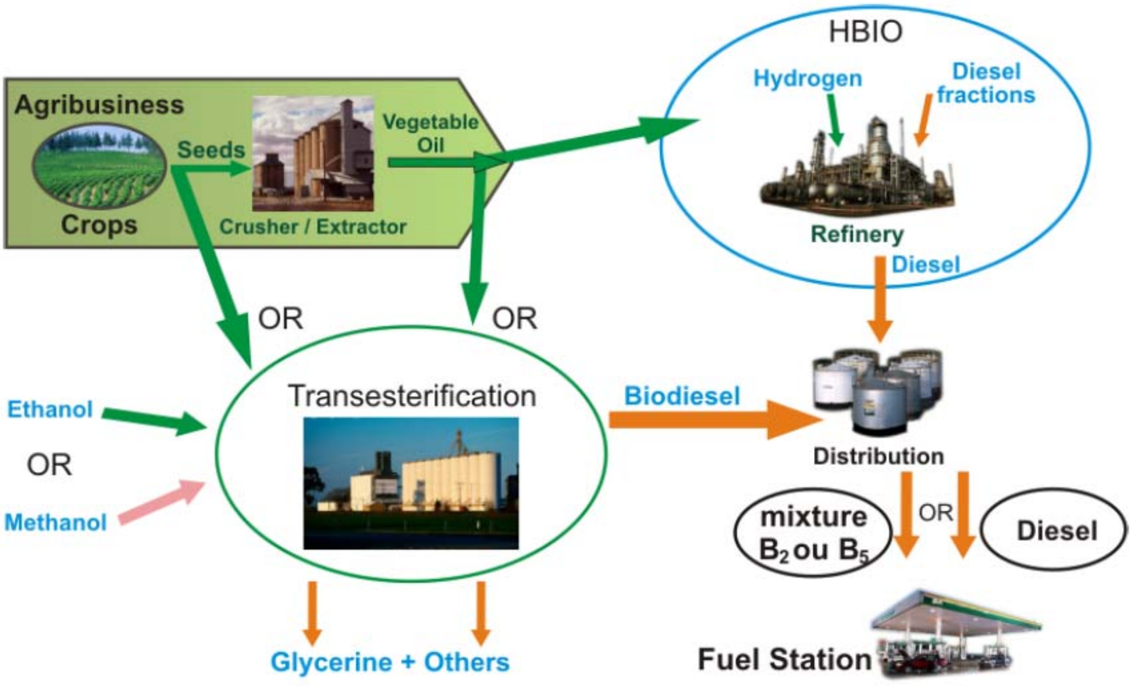
3.3.5.2 H-Bio – Petrobras

Petrobras, the national energy company of Brazil, in the spring of 2006 announced the development of its in-refinery natural oil processing approach, which it calls H-Bio. This is described as a new technique to refine low-sulfur diesel fuel from vegetable oil, and is the result of research carried out by the Petrobras Research and Development Center (Cenpes) in 2004 and 2005.

Petrobras says that it may use the technology to boost diesel production at its refineries. The technology handles vegetable oils, such as soybean oil, with diesel fractions in hydrogenation. They claim that the fuel can be made at traditional hydrocracking facilities and does not require new facilities, just adjustments to existing refineries. Figure 3.61 shows the complementary process between the H-Bio and biodiesel production. The new technology is said to use

5-10 percent vegetable oils. Testing is reported to have been conducted at Petrobras' Regap refinery in Minas Gerais state, and the new diesel could be phased in commercially over the next few years at additional refineries, and would reduce diesel imports by 15 percent a year since the start of production of H-Bio biodiesel at three refineries in the first quarter of 2008. The company also reported that industrial production at the first refinery, Repar in the southern Brazilian state of Paraná, started at the end-2006. The company has started industrial production tests for the fuel at the Repar refinery. Two other refineries, Regap and Refap, were expected to start producing H-Bio in 2007 and 2008, but were put on hold because of the rising raw material costs.

Figure 3.61 H-Bio and Biodiesel Complementary Process



Source: Petrobras

Petrobras gives no details on how much it costs to make the new diesel, but did announce that they could invest US$ 38 million to produce the new fuel at the three refineries. According to a statement issued by Petrobras, the H-Bio plant will reduce import needs by 250 million liters a year. The second stage of the program is budgeted at US$ 23 million to convert another two refineries to produce H-Bio by end-2008, which could reduce diesel imports 25 percent from the 2006 import projections. Nexant infers from this information that investment costs are about $0.60 per annual gallon of H-Bio capacity, as contrasted with typical total project investments of over $2.00 per annual gallon for conventional FAME capacity.

Petrobras is buying biodiesel made conventionally from vegetable oil in Brazil as the economy began mixing it with standard diesel fuel in 2008, but Petrobras has stated that it is working on other proprietary technologies to make the use of crops, such as soybeans, cheaper when used for producing fuels.

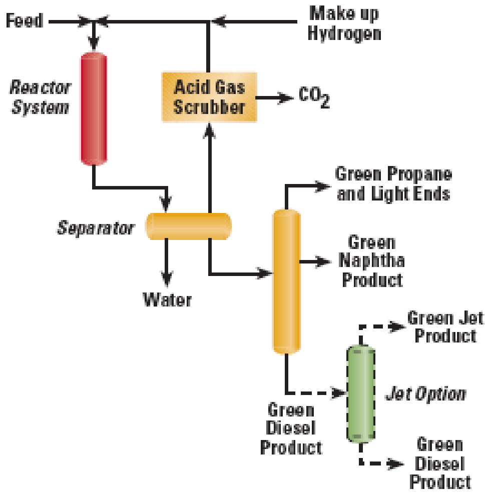
3.3.5.3 *Ecofining – UOP*

UOP LLC, in conjunction with Eni S.p.a, has commercialized their Ecofining process which converts vegetable oils and wastes to green diesel fuel. The process uses conventional hydroprocessing technology focused on producing a high quality product which will be compatible with the fuel infrastructure already in place.

The Ecofining process, developed by UOP along with Eni, deoxygenates biofeedstocks with the addition of hydrogen to create a highly stable green diesel fuel. The process works with many different types of biofeedstocks, ranging from pretreated vegetable oils, like rapeseed, canola, soybean, palm and jatropha to the second generation feedstock options such as algae oils and cellulosic feeds. Ecofining can also process animal fats such as tallow for feedstock to produce green diesel.

The process hydrogenates triglycerides and/or free fatty acid feedstocks like vegetable oils and animal fats. The ensuing paraffins then isomerize in order to create the high quality hydrocarbon, green diesel. The Ecofining processes utilized deoxygenating and isomerization catalysts which are supplied by UOP. The final diesel product has a higher octane value, low density, lower cloud point and lower emissions than biodiesel or the traditional petroleum diesel. The Ecofining process can also produce a paraffinic green jet fuel stream along side the green diesel if the company wanted. Figure 3.62 shows the process flow diagram of the Ecofining process.

Figure 3.62 Ecofining Flow Diagram



Source: UOP

The green diesel fuel product is compatible with traditional diesel fuel, but saves over 50 percent of greenhouse gas (GHG) and NOx emissions. It can work as a drop in replacement for its petroleum counterpart, or as a blendstock which will enhance the quality of the existing diesel pool. Green diesel is chemically similar to petrodiesel and can therefore be used in the existing tanks, pipelines, trucks, pumps and vehicles without much change, which will save expenses, such as capital and operating costs, in the future as the demand for renewable fuels grows. Table 3.32 displays the diesel fuel property comparison between petroleum diesel and the UOP/Eni Green Diesel.

Table 3.32 Diesel Fuel Property Comparison

	Fossil Diesel	Green Diesel
Oxygen Content (%)	0	0
Specific Gravity	0.84	0.78
Cloud Point, (°C)	-5	-20 to +10
Cetane	40-52	70-90
Sulfur (ppm)	< 10	< 2
Energy Density (MJ/kg)	43	44
Polyaromatics (Vol %)	8-12	0
Oxidative Stability	Baseline	Baseline

Source: UOP

3.3.6 FCC Cracking

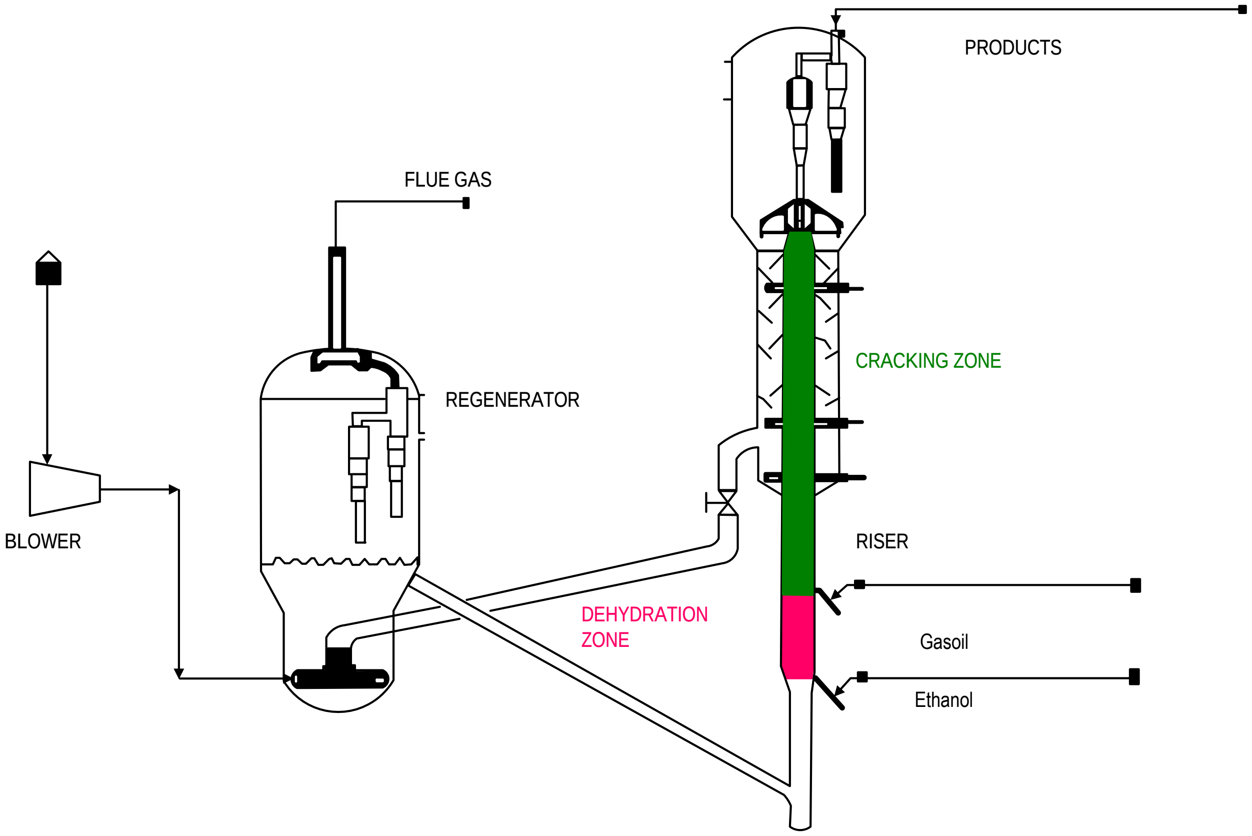
Petrobras has experimented with adapting FCC units to convert biomass and other biofuels materials to hydrocarbons that are more compatible with petroleum and petrochemical operations and with conventional vehicle fueling systems. Through tests carried out in an FCC pilot riser they have shown how FCC technology can be modified to process many different renewable raw materials, including ethanol, vegetable oils, and straw. Ethanol was shown it was easily dehydrated to produce ethylene, by co-processing with regular FCC feeds, such as Heavy Vacuum Gasoils, and typical catalysts. Yields are typically as high as those obtained commercially in dedicated units, of around 95 percent (stoichiometric), producing an enriched ethylene fuel gas. Vegetable oils are also a potential source of high octane gasoline or light olefins, using special ZSM-5 catalysts.

The dehydration of ethanol in an FCC unit is fast (less than 2 seconds), endothermic, and does not require special FCC catalyst. The mechanism of ethanol dehydration is thought to identical to the reactions described for the SD/Chematur technology described above in this section of the report. The FCC can be used flexibly to achieve different ends in a refinery. Both co-injection and separate injection in FCC risers have been examined by Petrobras. Ethanol segregation favors ethylene production, but ethane production is favored when ethanol is blended with the gasoil and both feeds introduced into the FCC riser at the same point. Results imply that the intimate contact between ethanol and gasoil feed interferes with the dehydration reactions and promotes some hydrogen donation from the gasoil feed to the dehydration products. Ethanol conversion to ethylene is increased when the ethanol is injected before the contact of catalyst with the main feed. This approach creates two different reaction zones:

- A dehydration zone at the bottom of the riser, where hot catalyst from the regenerator contacts the ethanol at a high catalyst-to-oil ratio and temperature
- A cracking zone, where the gasoil feed is processed

The system is illustrated in Figure 3.63.

Figure 3.63 Ethanol Dehydration in an FCC Unit
(Process Scheme)



Source: Petrobras

In 1983, Petrobras had processed vegetable oils commercially in an FCC unit (REMAN in the State of Amazonas). Soybean oil was converted with the aim of increasing gasoline production in the refinery. Although technically successful, the operation was not economically attractive because of the high vegetable oil prices. The resulting gasoline had a higher octane number and much lower levels of sulfur and nitrogen than that based on petroleum. The oxygen level of the product was negligible and it was reported to be as stable as any other naphtha from FCC.

However, feeding fats, oils, and greases to an FCC can be more economical in producing light olefins. Table 3.33 shows the results obtained in a DCR (Davison Circulating Unit) pilot riser FCC processing pure soybean oil under special conditions and using a ZSM-5 based catalyst, aimed at maximizing light olefins. The FCC operation can be tuned to maximize either propylene or ethylene. Higher reaction temperatures favor ethylene production, while propylene yield is maximized at more conventional FCC reaction temperatures, reaching 19 percent weight. The amounts of undesirable products such as LCO and Decanted Oil (DO) were minimized, but there is an inevitable production of considerable amounts of water, CO_2 and CO.

Table 3.33 Soybean Oil Processing in an FCC Pilot Unit

(Light Olefins Maximization)

Reaction Temperature	580	600	620
Yield, % wt/wt.			
Fuel Gas (except ethylene)	4.2	5.8	7.8
Ethylene	10.6	11.5	12.1
Propane	1.7	2.0	1.9
Propylene	19.3	18.2	16.7
C_4's	10.0	9.3	7.7
Gasoline (IBP-221 °C)	25.9	27.4	27.1
LCO (221 °C-344 °C)	5.6	5.8	5.5
Decanted Oil (+344 °C)	1.6	1.8	1.9
Coke	4.9	5.3	6.2
Water + CO+CO_2	16.2	12.9	13.1
% Aromatics in Gasoline (Chromat.)	87.3	90.0	92.2
Gasoline RON (Chromat.)	109.2	108.5	109.7
Source: Petrobras			

Source: Petrobras

Petrobras is aiming to also develop a catalytic fast pyrolysis in an FCC to convert biomass such as sugarcane straw to hydrocarbons. Burning sugarcane straw in the fields for harvest is a growing problem in Brazil, so converting it to fuels would represent a multiple opportunity. CENPES (the Petrobras Research Center) has test riser unit adapted to convert straw or bagasse. One challenge is the high oxygen content of straw or bagasse (around 40 percent), which results in water vapor, CO, and CO_2 production. Nonetheless, they report success in co-feeding finely ground straw to the riser and obtaining good yields of hydrocarbons.

3.3.7 FAME – Homogeneous Catalyst

A typical Fatty Acid Methyl Ester (FAME) process is described below.

3.3.7.1 Feed Pretreatment

Feeds containing high levels of free fatty acids (FFAs - typically 4-10 percent) are problematic since these acids react with the basic catalyst, increasing its consumption and forming soaps that must be removed. Such feeds are typically subjected to esterification with methanol in the presence of an acid catalyst, such as sulfuric acid, to convert the FFAs to methyl esters. The effluent from the acid-catalyzed esterification is processed in base-catalyzed transesterification for conversion of the triglycerides. When FFA levels are modest (ca. 1.5 percent or less), the feedstock is usually pretreated by caustic refining to remove the FFA prior to use as transesterification feed.

3.3.7.2 Esterfication

A process flow sheet for conversion of crude vegetable oil to biodiesel is shown in Figure 3.64. Crude, degummed vegetable oil is fed from the day tank, preheated to 70°C, and sent to the retention tank where it is contacted with a 9.5 weight percent caustic soda solution and next with preheated (70°C) wash water. The two-phase mixture from the retention tank is separated in a centrifuge, with the wastewater sent to a settling tank within the battery limits for pretreatment ahead of offsite biological treating. Caustic-refined oil from the centrifuge is freed of water in a vacuum dryer. Water removed overhead is condensed and sent to treating. Dry, refined oil goes to intermediate storage.

Dry, refined oil undergoes a two-stage esterification reaction. Fresh and recycled methanol is fed to the mix tank, where an alkaline catalyst (typically potassium hydroxide) is added. Alternative catalysts are sodium hydroxide and sodium methoxide. There is much literature claiming the superiority of alkoxide catalysts. A 2:1 molar excess of methanol is used, and catalyst is maintained at about 10 weight percent relative to the methanol feed. This mixture is sent along with the oil to the agitated first-stage esterification reactor, which is heated by a steam coil. Effluent from the first stage is separated in a settler, with the upper organic phase going to the second-stage esterification reactor and the lower aqueous phase going to glycerin recovery. Additional methanol and catalyst are fed to the agitated second-stage esterification reactor, also heated by a steam coil, and the effluent is sent to a second separator. The aqueous phase from the settler goes to glycerin recovery, while the organic phase is sent to ester washing.

Improvements to the esterification reaction have been proposed. One approach is to use an inert co-solvent to generate an oil-rich, one-phase reaction system, with the claimed benefit of much faster reaction times resulting from eliminating mass-transfer limitations in the conventional two-phase system. A single reaction phase can also be created by using supercritical methanol as both solvent and reactant. This approach also greatly reduces reaction time and does not require catalyst. The reaction runs at only 35°C, versus about 60ºC, but requires operation at about 35 MPa compared to 0.1 MPa (atmospheric) for the conventional process.

3.3.7.3 Product Recovery and Cleaning

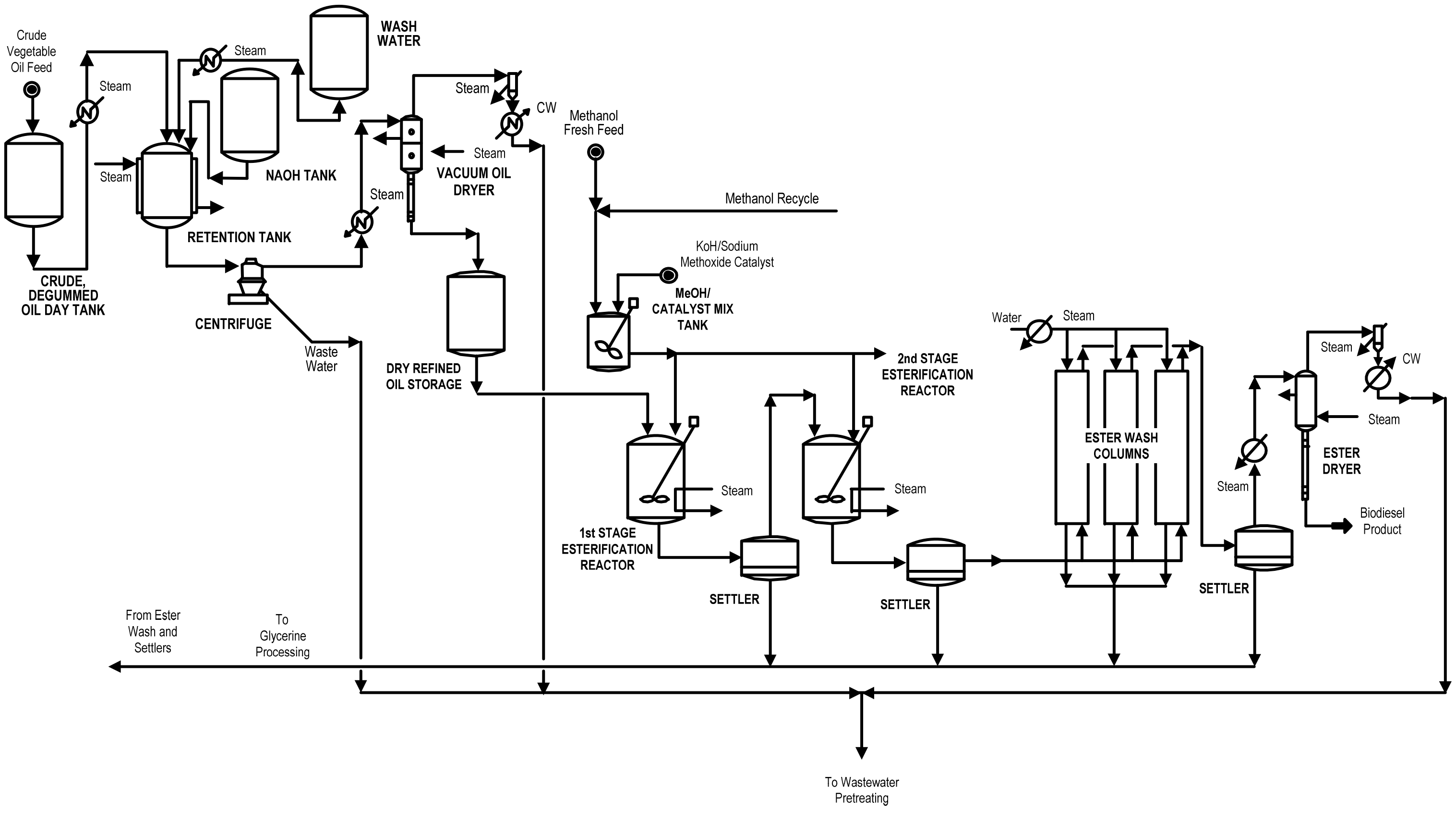
The methyl ester is contacted with water, preheated to 70 °C, typically in three parallel counter-current wash columns. The aqueous phase from the bottom of the wash columns goes to glycerin recovery. The tops of the wash columns go to a settler from which the lower aqueous phase is also sent to glycerin recovery. The organic phase from the settler is preheated, and next dried under vacuum in a steam-heated dryer. Water taken overhead in the dryer is condensed and sent to treating. Dry biodiesel product exits the bottom of the dryer to storage. The mass yield of biodiesel on crude oil feed is about 96 percent, the net of a stoichiometric addition of methanol, byproduction of a nearly equal weight of glycerin, and various process losses due to free fatty acids and other miscellaneous factors. This yield depends however on the type of oil or fat feed, and on its condition (especially FFA content). FFA tends to form a soap phase as a byproduct, and this is generally a process problem, since the soap tends to concentrate in emulsions at oil-water interfaces.

Streams from various sources, collected in the crude glycerin hold tank, are fed to the glycerin recovery column. Here, a methanol and water mixture is taken overhead and methanol and water are further separated in the methanol dryer column. The overhead from the methanol dryer is condensed and recycled to esterification. The bottoms stream from the methanol dryer is sent to wastewater treating.

The bottoms stream from the glycerin recovery column is cooled and sent to a hold tank. It is next fed to the agitated acidulation tank. The stream is acidified by a stream of 10 percent aqueous hydrochloric acid to neutralize the catalyst and aid in breaking emulsions. The organic phase from the acidulation tank goes to a settler, where the upper organic phase, consisting of FFAs, is sent to storage. Bottoms from the settler and bottoms from the acidulation tank, containing about 80 weight percent aqueous glycerin, go to a hold tank, typically prior to being sent offsite for concentration and purification in a larger-scale shared facility.

Wastewater streams from various points in the process, as detailed above, are combined in a surge tank before being fed to a settler for pretreatment. The overhead stream from the settler is comprised of fats and oils, which are sent to solid waste disposal. Wastewater containing methanol, soap, and glycerin from the bottom of the settler is sent for biological treatment outside the battery limits.

Figure 3.64 Biodiesel (Fatty Acid Methyl Esters) Process



3.3.8 FAME – Heterogeneous Catalyst

The new Axens - IFP Esterfip-H heterogeneous (solid) catalytic, continuous biodiesel process is aimed at producing cleaner biodiesel and byproduct glycerin at lower cost than conventional FAME processing. The process was developed by the French Institute of Petroleum (IFP) and commercialized by Axens. The current process uses a heterogeneous catalyst, a magnesium-aluminum oxide (spinel) mixed oxide of two (non-noble) metals. Using heterogeneous catalysts eliminates the need for catalyst recovery and washing steps and associated waste streams required by processes using homogeneous catalysts such as sodium hydroxide or sodium methylate.

Axens claims to produce biodiesel meeting or exceeding all international standards (EN 14214, ASTM D6751). Other main advantages claimed by Axens are the following:

- Exceptionally high purity glycerin by-product stream (no salt contamination)
- Lower catalytic cost compared to conventional liquid (homogeneous) catalysis
- No waste production of low value fatty acids leading to a very high yield of ester per ton of oil
- No consumption and therefore no handling of hazardous, corrosive chemicals
- Simplified process scheme: no acid injection, no water wash
- No sophisticated, long-delivery items or materials of construction
- Technology is backed by the ongoing R&D effort of IFP, on of the world's largest independent research organization in the field of motor fuels and their applications
- Since the active catalytic phase remains in the reactor while oil and methanol reactants flow through, three main differences with the conventional homogeneous catalysts are achieved:
  - The usual side reactions involving the catalyst, such as soap formation, cannot occur
  - No catalyst recovery nor aqueous treatment steps required
  - High yields of methyl esters, close to the theoretical values

The only product purification needed involves separating methyl esters from glycerol, which occurs spontaneously with removal of any unreacted methanol - no acid neutralization or water wash is required.

References given by Axens for projects being developed are shown in Table 3.34.

Table 3.34 Esterfip-H Project References

Customer	Location	Capacity t/yr/gallon/yr	Start-up Date
Diester Industrie	Sète (France)	160,000/50 million	Q1 2006
Confidential	Scandinavia	160,000/50 million	Q4 2006
Confidential	Southern Europe	50,000/15 million	Under design
Confidential	USA	166,000/50 million	Under design
Mission Biofuels	Malaysia	250,000/75 million	2009

The process uses two successive fixed-bed reactors, with glycerol separation shifting the equilibrium. Esters and glycerol are separated in a settler. Biodiesel is recovered after the final recovery of methanol by vaporization under vacuum, and is next purified to remove traces of glycerol. Esterfip-H exhibits very high biodiesel yields and directly produces salt-free glycerol at purities exceeding 98 percent. The quality of the glycerol yield adds to the economics of the process.

Esterfip-H process is comprised of three main functional blocks:

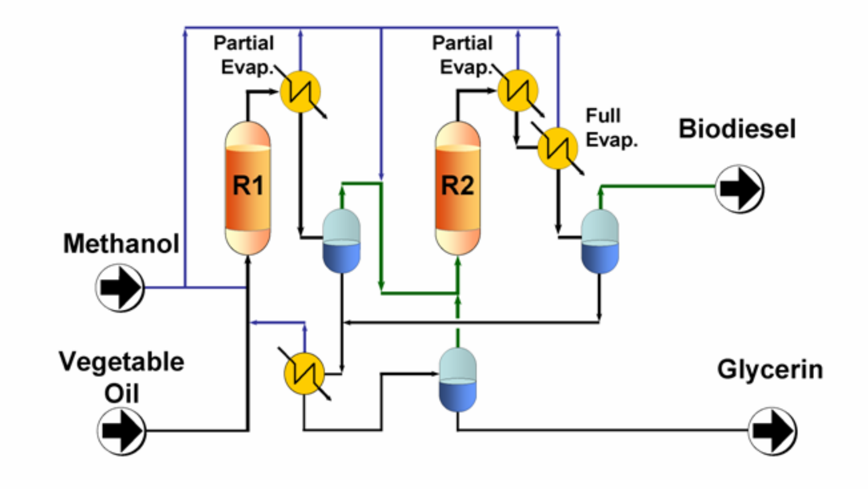
1. Feed Preparation and Methanol Mixing
2. Reaction
3. Product Separation

The oil feed is appropriately pretreated. The methanol feed stream is composed of fresh methanol make-up (depending on the net consumption) and recycled methanol. The mixture pressurized and heated to reaction temperature prior to entering the first reactor.

High efficiency depends on high conversion of triglycerides in the oil to esters, while minimizing di- and mono-glyceride production. This is achieved by maintaining a stoichiometric excess of methanol and by a two reactor scheme with an inter-reactor glycerol removal, which serves to drive the reaction towards maximum ester production.

The two reactors are fixed-bed type operating in liquid phase and are loaded with the same solid catalyst STR111. A partial evaporation of the methanol excess at the outlet of the first reactor allows for the separation of the glycerin already produced from the unconverted oil and ester phase. Figure 3.65, as provided by Axens, schematically illustrates the process.

Figure 3.65 Axens Esterfip-H Process Schematic



Source: Axens, 2006

Diester Industrie, a French company that pioneered biodiesel production, is building a new biodiesel unit in Venette, near Compiègne, France based on the Esterfip-H process. The new unit has a capacity of 100 thousand tons per year (about 30.2 million gallons per year US), and doubles the site's current production. Diester contracted with Technip in 1996 for the construction of a biodiesel plant in Rouen, France. In 1994, Diester awarded Technip a contract to build a 160 thousand tons per year (about 48.3 million gallons US) plant in Sète—also based on the Axens process.

3.3.9 FFA Pretreatment

Pretreatment systems for free fatty acids (FFAs) are being utilized more in recent years as more cheap feedstocks are being used for biodiesel production. Inexpensive feedstocks are being used more as an alternative in order to avoid high priced virgin vegetable oils. The pretreatment systems can clean up less than desirable feedstocks and can eventually improve the output of biodiesel for producers.

The main component in fats and biodiesel are fatty acids where in virgin soy oil, three fatty acid molecules form an ester with glycerin. The fat molecule is then broken down by transesterification with sodium methoxide as the catalyst and produces three molecules of biodiesel. On the other hand, if the fat molecule is broken, such as when oils are used for frying, the fatty acid molecule breaks free in the solution. The catalyst then comes together with the free fatty acid molecule and forms soap. The formation of soap also makes more water which can hydrolyze the triglycerides and create more soap. The more soap generated in the biodiesel tanks, the more washing and purification of the biodiesel product is required for the producer. The chemical reaction which occurs during the transesterification process is not able to convert free fatty acids and therefore inhibits the overall reaction and creates soap in the process.

High levels of FFAs also produce less amounts of biodiesel from every gallon of oil which the biodiesel producers buy. Hence, cheap feedstock are inexpensive for a reason, because they have high levels of undesirable components like free fatty acids that make it hard to make biodiesel. The majority of alternative feedstocks need pretreatment because of their high FFA content. There are ways for waste vegetable oils and other low cost feedstocks to be better suited for the production of biodiesel. New systems can distill free fatty acids and leaving behind triglycerides which can then be made into biodiesel. Table 3.35 displays the ranges of FFA that are commonly found in biodiesel feedstock. Ordinarily, if the FFA level is less than one percent, the FFAs can be ignored.

Table 3.35 Ranges of FFA in Biodiesel Feedstock

(Percent)

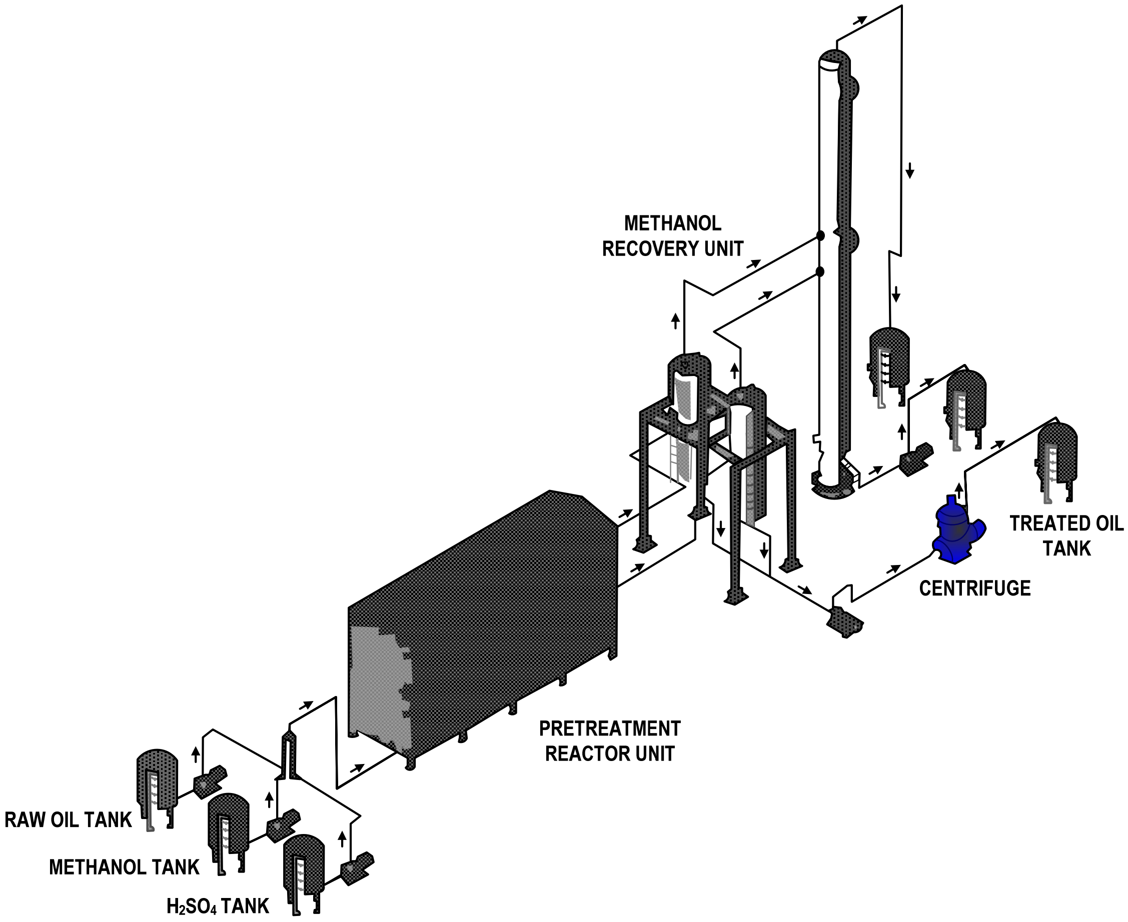
Refined Vegetable Oils	< 0.05
Crude Vegetable Oil	0.3-0.7
Restaurant Waste Grease	2-7
Animal Fat	5-30
Trap Grease	40-100

If the feedstock being used has a FFA content of 5-30 percent or higher, it is critical to convert the free fatty acids to biodiesel or the overall process yield will be lower than expected. Four techniques to change FFAs to biodiesel are:

- Enzymatic methods – require expensive enzymes but are less affected by water
- Glycerolysis – involves adding glycerol to the feedstock and heating it to a high temperature, e.g., 200°C, with a zinc chloride catalyst typically. The FFAs react with the glycerol to create mono- and diglycerides, producing a low FFA feed which can be processed with the usual alkali-catalyzed techniques. A disadvantage to this technique is the use of high temperatures with a slow reaction while the advantage is the use of no methanol during pretreatment in order for water to be formed by the reaction, which is vaporized and vented from the mixture
- Acid Catalysis – utilizes a strong acid, e.g., sulfuric acid, for the catalysis of the esterification of the FFAs and the transesterification of the triglycerides. The esterification reaction of FFAs to alcohol esters is fast and goes to completion in approximately one hour at 60 °C while the transesterification reaction of the triglycerides is slow in comparison, usually taking a couple of days for completion. Increasing the temperature of the transesterification step to 130°C can speed up the reaction; however it will still take up to 30-45 minutes to complete. The overall process does not create soap since no alkali metals are used but water is generated in the reaction and remains in the mixture and finally stops the reaction well before it comes to completion if not treated
- Acid catalysis followed by alkali catalysis – uses each technique to carry out the process is it more capable of, overcoming the reaction rate problem. Acid catalysis is used for the pretreatment of high FFA feedstocks because it converts FFAs to methyl esters fast. The alkali catalyst is added to the process when the FFA content is down to about 0.5 percent for the conversion of triglycerides to methyl esters. Water is still generated in the pretreatment phase of the process and is the main disadvantage of the technique

SRS Engineering Corporation developed a scalable, continuous flow, skid mounted system that can be in the front end of any existing biodiesel system and can efficiently convert FFA into useable oil with no yield losses. Their FSP-Series Acid Esterification pretreatment system is able to handle many high free fatty acid feedstocks. As an alternative to removing FFAs from the feedstock, the acid esterification process by SRS Engineering uses sulfuric acid to make the FFA merge with methanol to produce biodiesel in small amounts and neutral oil. The methanol and sulfuric acid mix together and then put into the oil stream. The mixture is heated and reacted under temperature and pressure. The modified waste additive is added after the esterification process and then blended with an oil-methanol stream with cooling at the same time. A light and heavy layer form and are separated by a specially designed separator where the light layer has the free fatty acids and is treated to be converted to usable oils. The methanol is then recycled into the process while the usable oils are centrifuged in order to be ready for transesterification. The mixed oil and methyl esters from the pretreatment system can go directly into a biodiesel plant's transesterification system. The process is scalable and is able to have flow rates ranges from 500 thousand to 150 million gallons per year. Figure 3.66 displays the SRS Engineering pretreatment system process flow diagram.

Figure 3.66 SRS Engineering Pretreatment System Process Flow Diagram



Source: SRS Engineering Corporation

The pretreatment system is installed in between the oil holding tanks and the transesterification reactor in the biodiesel plant. In order to lower heat loss, the system is installed as close to the reactor as possible, therefore lowering the energy costs of the transesterification reaction since the feedstock needs to be heated to convert the FFAs and remove water. The treated feedstock has to be generated and placed into the esterification process all in one step which conserves energy because the energy that is used in the esterification step can be carried through to the next step because of the proximity of the system to the transesterification reactor.

The SRS Engineering pretreatment has its advantages and disadvantages. A disadvantage of their acid esterification process is the generation of a small amount of water which encourages the production of soap in the transesterification process. Therefore, the water needs to be removed before the rest of the oil can be generated into biodiesel. The company has built a distillation system in order to remove the water from the pretreated oil and prevent the formation of soap, which prohibits the esterification process. The process is done in two steps with two different temperatures and pressures for the final conversion where water is removed to speed up the reaction during the halfway point of the process. Some advantages of the FSP-Series pretreatment system are no yield losses, approximately a 1-to-1 ratio producing 100 gallons of biodiesel from 100 gallons of oil, energy efficient, able to utilize 15 percent FFA or higher, and lowers the risk for high FFA feedstock environmental emissions.

3.3.10 Bio Co-Solvent Process

The BIOX co-solvent process is a new biodiesel process developed by Professor David Boocock of the University of Toronto. BIOX is reported to have been successfully demonstrated in a laboratory and pilot plant scale. Boocock observed that kinetic data for base-catalyzed transesterification (transmethylation) had been previously misinterpreted. He found that methanolysis is slow (hours of reaction time required) because two phases comprise the initial reaction mixture, and therefore, the reaction is mass transfer limited. Selected cheap, recyclable, inert co-solvents generating an oil-rich one-phase system solve this problem. A number of cosolvents were demonstrated. In BIOX, the reaction is 95 percent complete in ten minutes at ambient temperatures, making continuous processing feasible. The acid catalyzed process, which, as discussed herein, is required when the substrate contains fatty acids, is complete in minutes rather than hours.

The process uses more methanol to increase the polarity of the mixture, which maintains the ionization of the catalyst. As is common, for substrates containing FFAs, BIOX first uses a one-phase acid-catalyzed step to convert FFAs, before using base catalysis to convert the triglycerides. In the two-step process, it takes about 30 minutes to convert FFAs at close to the boiling temperature of methanol (60°C). The base-catalyzed step is complete in seconds. With a recycle stream of methanol and a co-solvent, the latent heat of condensation is used to heat the incoming feedstock.

Because of its features, the process is able to deal with lower cost animal fats and greases, and used vegetable oils and waste greases. With these feeds and reduced processing costs, it is claimed that the total cost of production can be cut by as much as 50 percent, making biodiesel competitive with petroleum diesel. BIOX process requirements compared to conventional

FAME processing (e.g., from de-gummed soybean oil in the mid-western United States) are shown in Table 3.36. The BIOX process has lower potential feed costs but somewhat higher utility costs than conventional FAME processing.

Table 3.36 BIOX Process Requirements

Input	Requirement/Ton Biodiesel	
Feedstock - kg	1,000 waste oils (15% FFA)	1,037 soybean oil (<1.5% FFA)
Steam - kg	1,490	710
Electricity - kWh	19.7	28.9
Methanol -kg	110	89.5
Caustic soda (50%) - kg	33	4.6

Source: Prof. D. Boocock, University of Toronto.

There are no BIOX plants in operation yet other than their pilot plant.

3.3.11 Supercritical Processing

Supercritical processing uses relatively high temperatures and pressures so that the reaction times can be very short. It produces a fatty acid ester from oils and fats, but through a process quite different from conventional FAME processing. There could be some concern about the final quality, particularly the toxicity, of the biodiesel, because the temperatures are high enough for pyrolysis reactions to form non-ester products, but pyrolysis appears not to occur in the process.

Solvents explored so far include methanol, ethanol, propane and carbon dioxide. Experimental work indicates that the composition of the final biodiesel product is similar to that obtained in commercial processes. The process shown in Table 3.37 was reportedly complete in four minutes, with a yield of 98.5 percent biodiesel (traditional processes need processing times of several hours with yields of about 97 percent). There are as yet no demonstration or commercial supercritical plants in operation for biodiesel production, although a pilot plant is reportedly under development in Japan.

Table 3.37 Features of Supercritical Processing: Bio Super 3000

	Conventional Processes	Supercritical Processing
Reaction Time	1-6 hours	2-4 minutes
Reaction Conditions	0.1 MPa,30 – 65 ºC	>8.09 MPa, >240 ºC
Catalyst	Acid or Alkali	None
Free Fatty Acids	Saponified Products	Methyl Esters
Yield	Normal	Higher
Removal for Purification	Methanol, Catalysts, and Saponified Products	Methanol

Source: D. Kusidiana, S. Saka. “Biodiesel fuel for diesel fuel substitute prepared by a catalyst-free supercritical methanol.” Grad. School of Energy Science, Kyoto University, 2001.

3.3.12 FAEE (Fatty Acid Ethyl Esters)

Ethyl esters have been examined as an alternative to methyl esters for many years. FAEE (fatty acid ethyl esters) have the advantages of:

- Being completely derived from renewable materials
- Having a slightly higher energy density (less oxygen content per unit weight)

However, it has the disadvantage against FAME of being somewhat more difficult to process, and it is often stated in the literature that the primary reason for not pursuing FAEE is the higher cost of ethanol over methanol. Currently, however, if one compares ethanol with methanol on an energy-equivalent basis (methanol has much more oxygen in its molecule on a weight basis than ethanol, and therefore, less energy on a weight basis), then the difference becomes very small. On the other hand, ethanol’s market value is on the rise, while Nexant expects that methanol prices may be reduced by as much as half when it becomes valued relative to the price of stranded natural gas. Because of the relatively low price of ethanol in Brazil, biodiesel there is primarily FAEE.

Some of the notable activity in developing and engine-testing FAEE against petroleum diesel and FAME was conducted in Idaho from the mid-1980s through the mid-1990s by Dr. Charles Peterson, et al, of the University of Idaho, under Idaho State and United States DOE sponsorship. The latter phase of this work focused on FAEE made from waste hydrogenated soybean oil used for industrial potato frying (hence their term, HySEE, for Hydrogenated Soybean Oil Ethyl Ester). Peterson reported on his work and on a number of other short-term engine tests that were conducted worldwide in which FAEE and FAME were compared to diesel fuel. Peak engine power on the vegetable oil fuels ranged from 91 to 109 percent of that in the same engine operated on diesel fuel, with many reporting peak power equal to over 100 percent that of operating on diesel. Fuel consumption was generally slightly higher, reflecting the reduced energy content of the vegetable oil fuels. Thermal efficiencies are also generally reported to be slightly higher than for diesel fuel. However, injector coking was indicated to be significantly lower than with No. 2 diesel.

Table 3.38, from Brazilian and Australian sources, compares some methyl and ethyl ester and petroleum diesel fuel parameters. The slightly better performance indicated for FAME than for FAEE likely results from practical engine mechanical factors, despite the slightly higher theoretical heating value of FAEE over FAME. In any case, the differences are trivial.

Table 3.38 FAME and FAEE Compared to Diesel Fuel

Property	Methyl Ester	Ethyl Ester
Conversion (oil → biodiesel)	97.5%	94.3%
Total glycerin in biodiesel	0.87%	1.40%
Viscosity	3.9 – 5.6 cSt @40 °C	7.2% above methyl ester
Δ% Power versus diesel oil	2.5% less	4% less
Δ% Consumption versus diesel oil	10% more	12% more

Source: UNIFEI, Brazil, Australian Standard for Biodiesel Report, 2003

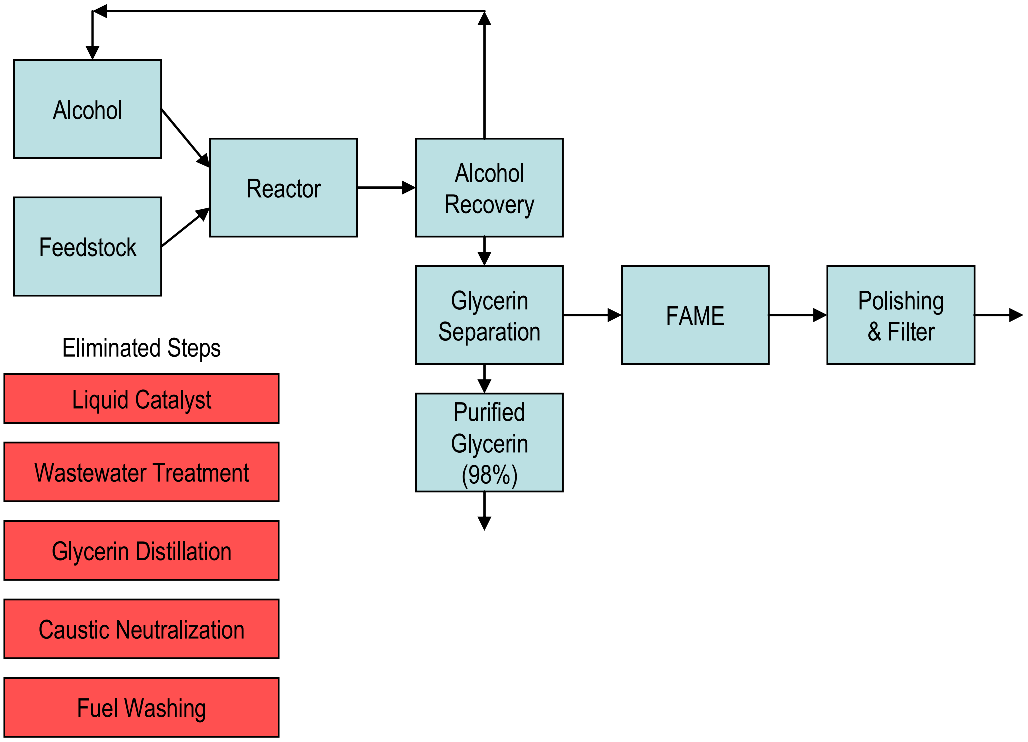
3.3.13 ENSEL™ – Benefuel (new catalyst for tranesterification reaction)

Traditional biodiesel "catalysts" are better described as chemical "reactants," rather than "catalysts," because they are destroyed during the refining process. Sodium and potassium hydroxides – the most common substances used to transesterify oils and fats into methyl esters - are consumed during production and must be washed out of the biodiesel crude. In addition to being discarded after each batch, caustic reagents must be neutralized with acid before the biodiesel can be recovered and then contaminate the glycerin byproduct with waste salts, which dramatically degrades its commercial value, as well as add costs to the biodiesel process.

Benefuel's unique dual metal catalyst (DMC) solves the problem of reactant waste and glycerin contamination. Benefuel, Inc. was formed from the merger of Gripp Industries and New Century Lubricants (NCL). The catalyst is an iron-zinc double-metal cyanide complex developed in collaboration with the National Chemical Laboratory (India) and manufactured by Süd Chemie India Pvt. Ltd. The solid catalyst is not consumed during transesterification, eliminating the need to wash catalyst from the FAME. This means that the ENSEL^{TM} process operates water-free, thus, eliminating the demand on limited water supplies. Typical biodiesel refineries can require about 3 to 5 gallons of water per gallon of biodiesel produced to wash out spent reactant.

Due to the unique nature of the DMC, methyl esters produced in a Benefuel refinery can be immediately blended (without washing) with petrodiesel to make biodiesel blends or used directly as the best B100 in the market. In addition to high-quality biodiesel, Benefuel's proprietary refineries also produce a high purity (98+ percent) technical-grade glycerin that has a multiple number of uses. The catalyst does not leach minerals into the glycerin phase and no water is required to process the effluent from the continuous flow reactors. After removing methanol, the glycerin and biodiesel separate naturally. A block flow diagram is shown in Figure 3.67.

Figure 3.67 ENSEL™ Process Flow Diagram



Source: Ensel™

The first commercial application of the ENSEL™ process will be in a biodiesel plant for Seymour Biofuels, LLC. Construction of the plant started in 2008 in Seymour, IN. It will have a capacity of 10 million gallons per year from unrefined soy oil and chicken fat.

3.3.14 Hydrothermal Upgrading (HTU)

3.3.14.1 Overview

The HydroThermalUpgrading (HTU) was originally developed by Shell Research back in the 1980s. Although the process has been around for a few decades, it is only recently that scientists are realizing its full potential as an alternative fuel production method. The process is especially significant because of its ability to process a wide range of wet biomass to produce a 'biocrude' mixture that can be converted to high-quality kerosene and diesel analogues. The diesel analogues can then be mixed with traditional diesel.

The ability to process wet biomass is a significant step in developing biofuel technology. Processing wet biomass increases the variety of feedstocks available for alternative fuel production.

Continuing research of the HTU technology is currently only performed by a Netherlands based consortium of TNO-MEP, Biofuel B.V. and the Waste and Energy Enterprise of the City of Amsterdam (AEB). Additional financial support is provided by Shell Nederland BV and Novem, the Dutch Energy Agency. The consortium runs a 100 kg/hr (wet) feed (8kg/hr of biocrude produced) pilot plant at TNO-MEP, Apeldoorn, The Netherlands. Not much is widely available about the details of the HTU process but a brief overview is provided in the following section.

3.3.14.2 Process Description

The key to biomass thermochemical liquefaction processes is the removal of oxygen. As biomass feedstock generally contains around 40-45 percent oxygen they are heated to facilitate the removal of oxygen. Oxygen removal increases the heating value and leads to a product with more hydrocarbon-like properties causing it to be immiscible with water.

The oxygen is either removed in the form of water or carbon dioxide. In the HTU process, reaction conditions cause oxygen to be removed in the form of carbon dioxide. Removal of water leaves carbon as a final product but removal of carbon dioxide leaves a product with a higher H/C ratio and therefore a higher LHV. The remaining organic hydrocarbon rich liquid is known as ‘biocrude’. Table 3.39 shows the properties and characteristics of biocrude.

The wet feedstock is heated and brought to reaction pressure by the pumps. Since most biomass HTU feedstocks have such properties that they do not flow readily through either pipes or shell of a conventional heat exchanger it is often preheated through direct injection of hot water.

The preheated feedstock is then sent to the HTU reactor where the reaction takes place at a temperature of 300-350ºC and a pressure of 120-180 bar in the presence of liquid water. The liquid effluent is then cooled to prevent any undesired reactions that could degrade the biocrude product. Gases produced in the reaction, mainly CO_2, are removed off the top of a separator while the two liquid phases of water and biocrude are also separated. The waste water is treated first by anaerobic digestion and then aerobic digestion. Biogas produced during anaerobic waste water treatment can be used as fuel in the fired heater. An after-treatment by aerobic digestion is usually required to remove minerals in the water stream in compliance with waste water discharge regulations.

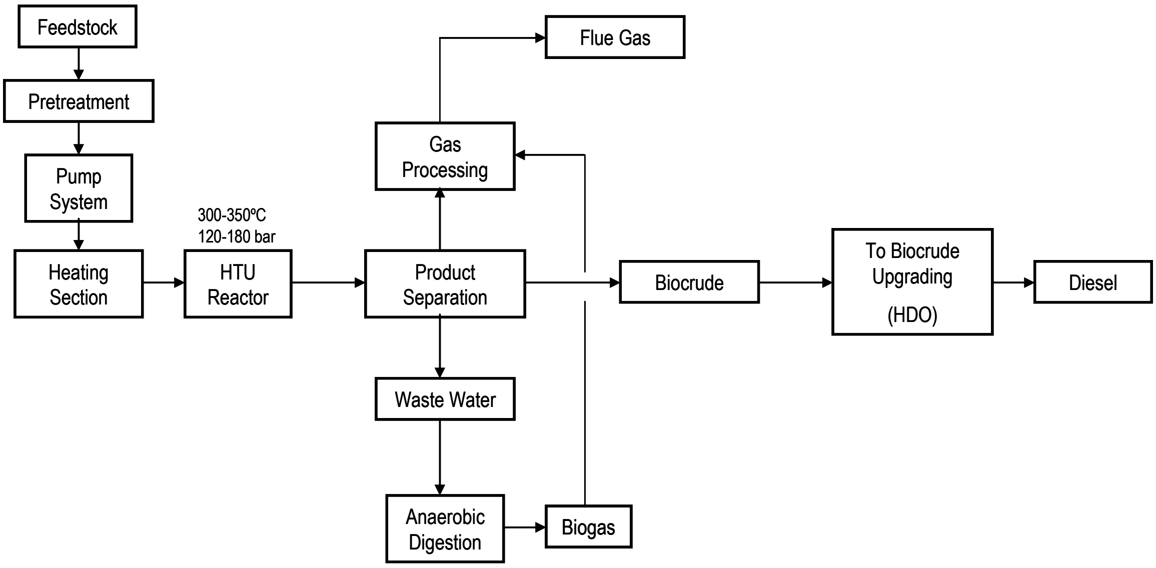
The biocrude product can then be upgraded locally or transported to other locations for upgrading. The lighter fractions of the biocrude are processed to become diesel fuel components using a well-known refinery technology called hydro-de-oxygenation (HDO). The HDO process removes oxygen as carbon dioxide by adding hydrogen to the biocrude. This liquid can then be blended with fossil diesel in any proportion without the need of engine or infrastructure modification. The heavy fractions of biocrude can be used to generate energy. A general process diagram of the HTU process is shown below in Figure 3.68.

Table 3.39 Properties of Biocrude

Property	
High Calorific Value	30 GJ/ton
Oxygen Content	10-18%w
H/C Ratio	1.1
LHV	30-35 MJ/kg
Liquid at	>80ºC
Immiscible with water	

Source: HTU® Biofuel BV

Figure 3.68 Block Diagram of HTU Process



Source: HTU® Biofuel BV

3.4 OTHER

A number of other approaches have been proposed that do not conveniently fit any of the paradigms covered above. Some of these are more advanced and otherwise important than others. Several of these are described below. Another development that might have been covered here but for lack of details available is the Algenol technology for making ethanol rather than lipids by photosynthesis using genetically modified algae in covered ponds. This technology is reported heading for a large-scale demonstration in Mexico.

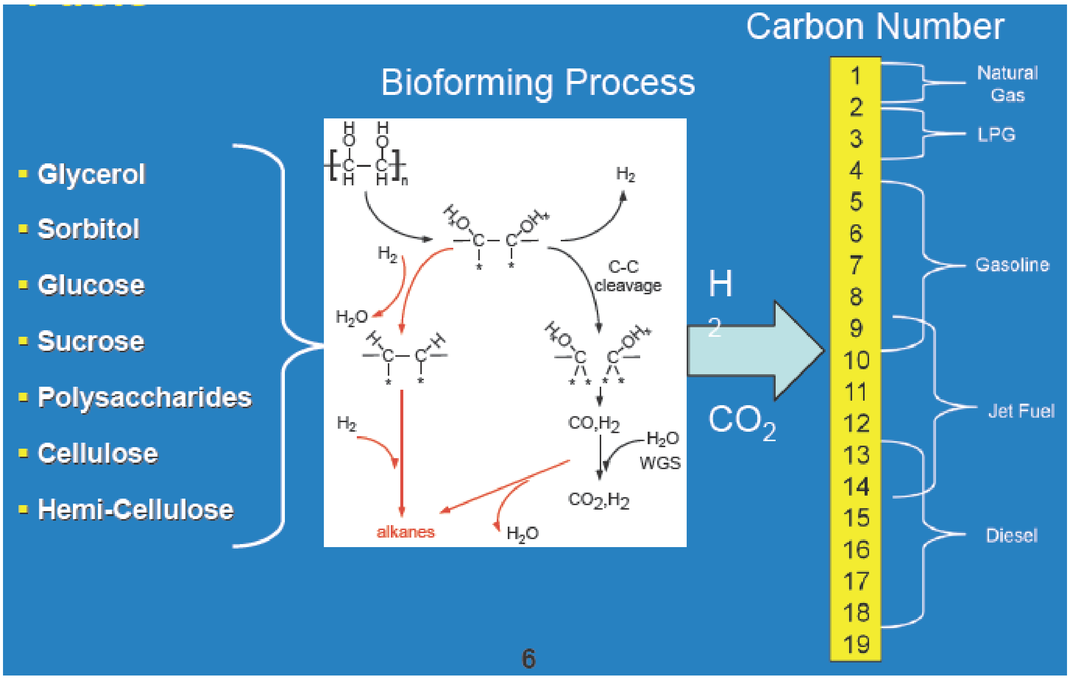
3.4.1 APR – Virent

Virent has developed an approach for catalytic conversion of sugar-based feedstocks to bio-gasoline utilizing their technology described as Aqueous-Phase Reforming (APR). This is part of a larger technology platform called the BioForming™ Process Platform, described as a "novel catalytic process technology for the conversion of biomass to conventional products". This is aimed at:

- Liquid fuels – gasoline, diesel, jet fuel, and alcohols
- Chemicals – glycols, aromatics, and alcohols
- Fuel gas – hydrogen, Supernatural^{tm} gas, and LPG

The range of potential applications, respecting feeds and products, is illustrated in Figure 3.69.

Figure 3.69 Virent Bioforming Process to Liquid Fuels



Source: Virent

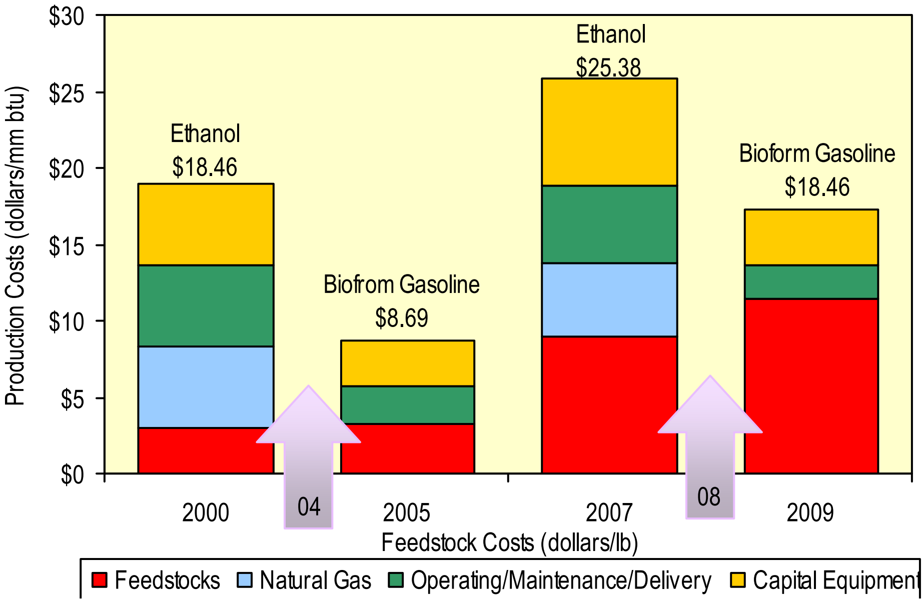
The process operates in the aqueous phase at low temperatures over a heterogeneous catalyst to convert dissolved carbohydrates to hydrocarbons that can be easily separated by phase in many cases. Some advantages claimed for bioforming to make gasoline are:

- Catalysts are not microbes – this avoids depending on fragile life forms and their biology; the products of cellulosic processing (e.g., sugars derived from biomass by hydrolysis, etc.) can be converted directly
- Energy balance – the developers claim that it produces gasoline with >50 percent higher net energy yield per acre than the ethanol process
- Water positive - bioforming makes water when taking the oxygen off of sugar streams does not require net process water
- Low energy for separations - gasoline immiscible in water, requiring minimal distillation.
- CO_2-neutral - low energy input and biomass based feedstocks offer near-zero carbon footprint

Virent claims to have produced high yields (over 55 percent feedstock energy) of green gasoline from glycerol, sorbitol, C_5 and C_6 sugar mixtures, corn syrup, and sucrose feedstocks. They also have demonstrated the exothermic nature of the integrated conversion process. They claim to have produced over 40 percent yields of heavy alcohols in other embodiments of the process, (contrasted with about 6 percent for fermentation processes). They also claim good yields for diesel and jet fuels.

Figure 3.70 shows the process economics presented by Virent comparing bioforming gasoline production with corn ethanol for two levels of corn prices. The bioforming takes the crude sugar made by hydrolyzing the cornstarch, and both routes are credited with DDGS sales. Plant scales are all 100 million gallons per year, and natural gas price is \$8 per MM Btu.

Figure 3.70 Virent Comparative Economics



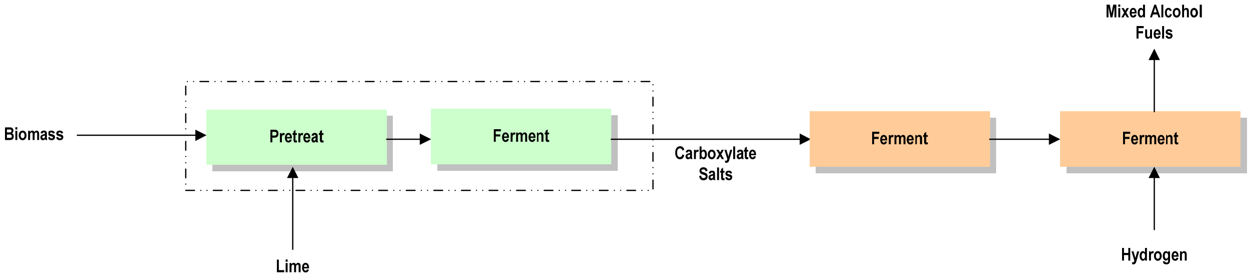
Source: Virent

3.4.2 MixAlco – Terrabon

Professor Mark Holtzapple of Texas A&M (TAMU) has developed a technology called MixAlco. The technology is being commercialized by Terrabon.

The process is a combined biological and chemical approach, going biologically from lime-treated lignocellulose via a mixed acid fermentation to carboxylate compounds, and next via chemical hydrogenation to alcohols, and next, possibly, to hydrocarbons by thermochemical catalytic conversion. The carboxylates can also yield esters. Figure 3.71 presents a process schematic.

Figure 3.71 MixAlco Process Schematic



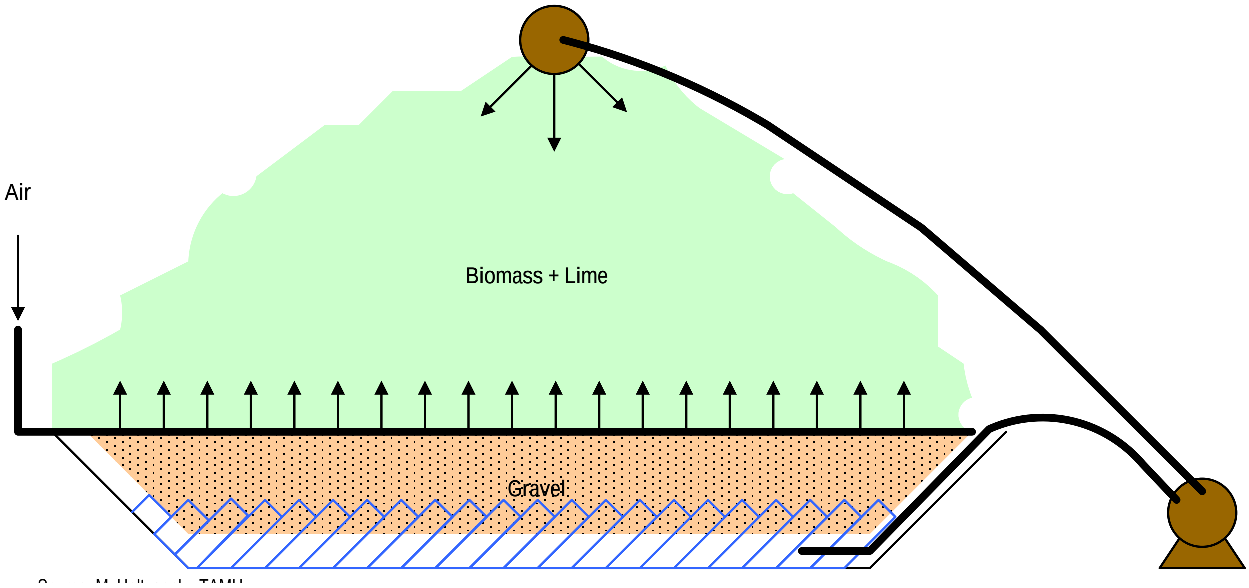
Source: M Holtzapple, TAMU

The technology can be applied to converting any biodegradable material (such as the organic fractions of municipal solid waste, industrial biodegradable waste, sewage sludge, agricultural residues such as corn stover, sugarcane bagasse and straw, cotton gin trash, manure, etc.) into a mixture of primary alcohols (e.g., ethanol, propanol, butanol) and/or a mixture of secondary alcohols (e.g., isopropanol, 2-butanol, 3-pentanol), and other useful chemicals, such as carboxylic acids (e.g., acetic, propionic, butyric acid), ketones (e.g., acetone, methyl ethyl ketone, diethyl ketone). The developers contend that, because of the many products that they say can be economically produced, this process is a true bio-refinery.

The process has been developed in a TAMU pilot plant at College Station, TX. It uses a mixed culture of naturally occurring microorganisms found in natural habitats such as the rumen of cattle, termite guts, and marine and terrestrial swamps. These organisms anaerobically digest biomass into a mixture of carboxylic acids produced during the acidogenic and acetogenic stages of anaerobic digestion, with inhibition of the methanogenic final stage. Other fermentation routes to ethanol and cellulosic ethanol use enzymes that must be isolated first to be added to the biomass to convert the starch or cellulose into simple sugars, followed then by yeast fermentation to ethanol. This process does not add such enzymes as these microorganisms make their own.

The anaerobic digestion of the biomass to convert it into a mixture of carboxylic acids lowers the pH of the mass controlled by adding a buffering agent (e.g., ammonium bicarbonate, or calcium carbonate [lime]), which yields a mixture of carboxylate salts. The lime treatment design is illustrated in Figure 3.72. Methane production would be the natural final stage of anaerobic digestion, but it is inhibited by the presence of the ammonium ions or by the addition of an inhibitor (e.g., iodoform). The resulting fermentation broth containing the produced carboxylate salts must be dewatered. This is achieved efficiently by vapor-compression evaporation. Any further chemical refining of the dewatered fermentation broth depends on the final chemical or biofuel product desired.

Figure 3.72 MixAlco Lime Pretreatment Illustration



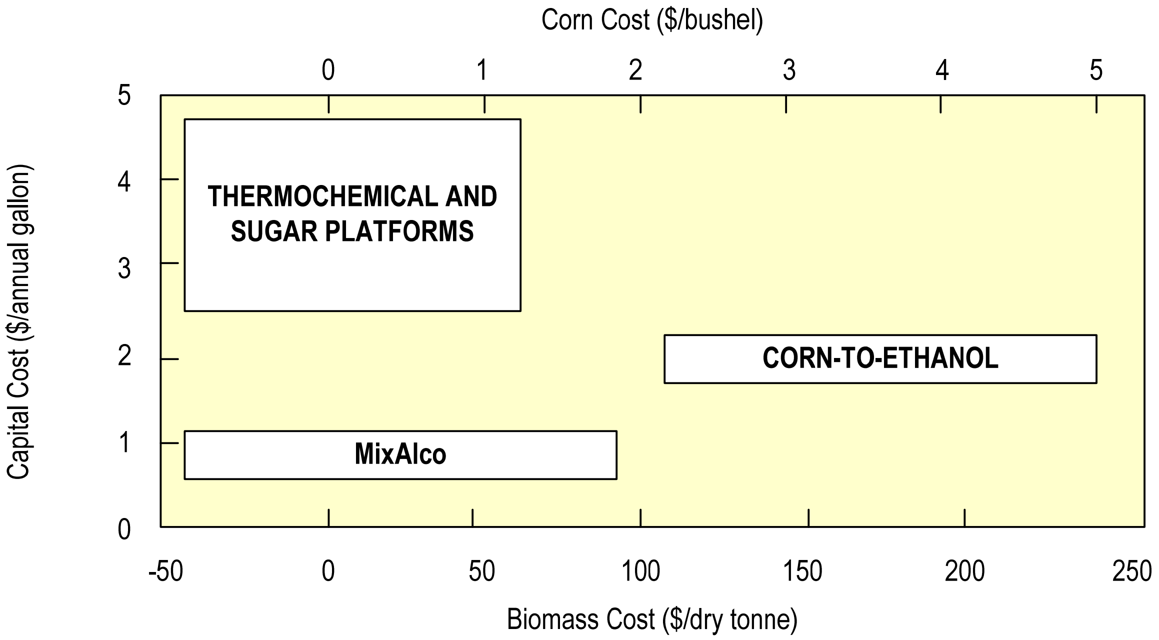
Source: M Holtzapple, TAMU

The condensed distilled water from the vapor-compression evaporation system is recycled back to the fermentation stage. If raw sewage or other waste water with high BOD is used as the water for fermentation, the condensed distilled water from the evaporation can be used economically in other ways. Thus, the process can also serve as a water treatment facility, while producing biofuels and chemicals.

Because the system uses a mixed culture of microorganisms (described by Prof. Holtzapple as "coming from dirt"), besides not needing enzyme addition, the fermentation requires no sterility or aseptic conditions, a major cost-saving feature. Savings in the front end of the process, where volumes are large, allows flexibility for further chemical transformations after dewatering, where volumes are small.

The developers claim large capital and operating cost advantages against other routes to alcohol fuels, as partly illustrated in Figure 3.73.

Figure 3.73 MixAlco Capital and Feedstock Advantages



Source: M. Holtzapple, TAMU

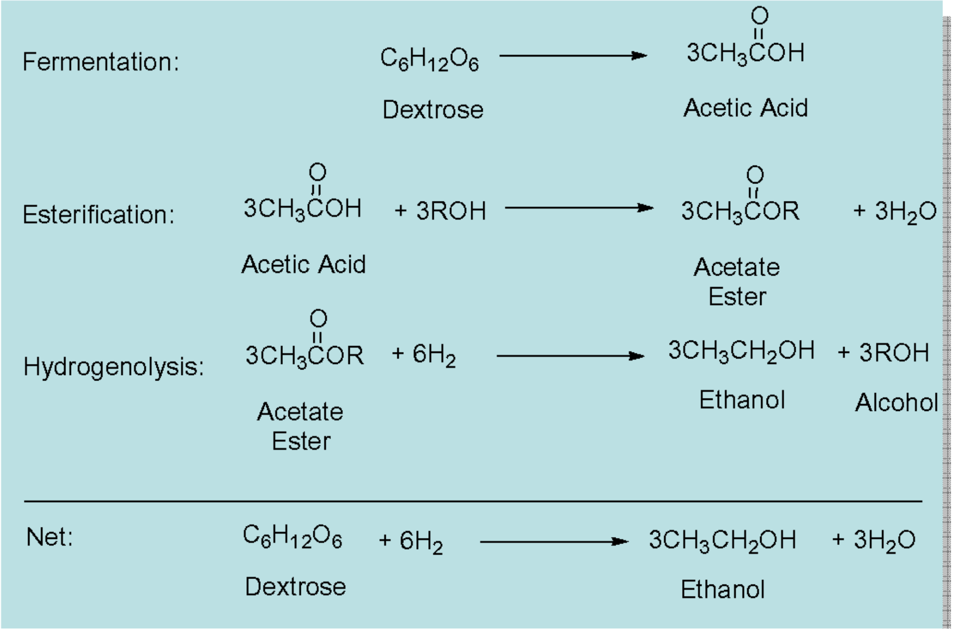
3.4.3 Zeachem – Ethanol via Acetic Acid

ZeaChem Inc. is a privately held company, founded as a partnership in 1998 and incorporated in 2002. It commercializes improved technology for biofuels, chemicals, and agricultural byproducts from renewable resources. ZeaChem has had significant public support for its developments. Aside from US DOE grants, the company entered into a formal joint development agreement with the Sugar Research Institute (SRI) in Queensland, Australia. Its work on an $800 thousand project for ethanol production from sugar cane molasses was successfully completed in 2003, which demonstrated ethanol yields from sugarcane of between 85 and 95 percent. Carbohydrate fermented to intermediate lactic acid can produce a protein by-product that is claimed to be a valuable aquaculture feed.

ZeaChem proposes an indirect method that is radically different from conventional fermentation approaches to producing fuel ethanol from renewable resources, and ZeaChem claims, with very high yields from carbon. Sugar fermentation and biomass gasification to syngas processing are combined in a novel way to preserve carbohydrate carbon in the ethanol product, while lignin and other non-fermented fractions contribute their mass and /or energy to forming ethanol via hydrogenation chemistry.

The core chemistry can be broken down into three steps, as illustrated in Figure 3.74, with dextrose as the fermentable carbohydrate.

Figure 3.74 Indirect Ethanol Production Route



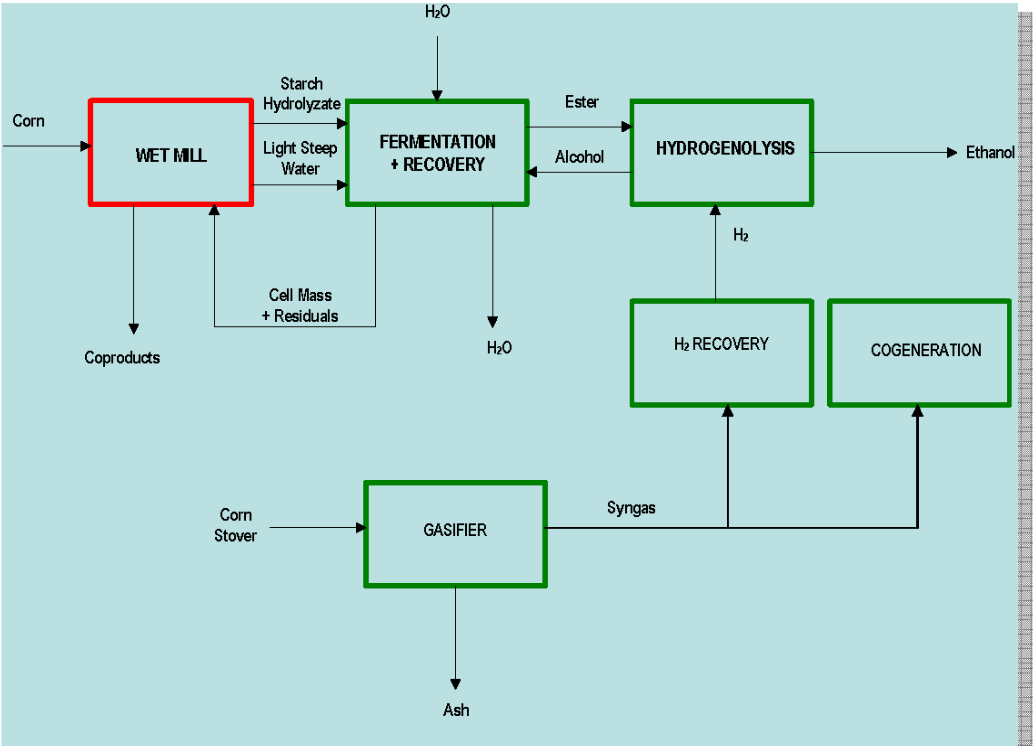
Source: ZeaChem, Inc.

First, homoacetogenic fermentation produces acetic acid from carbohydrate at near 100 percent carbon yield. Homoacetogens micro-organisms are well studied, and many wild-type strains are known to ferment both five and six carbon sugars. Therefore, there is potential to use genetic modification to have these organisms convert cellulose and hemicellulose from biomass to acetic acid.

In the second step, acetic acid is esterified with an alcohol to produce an ester. Esterification is a widely practiced high volume industrial chemical process technology. For example, Eastman Chemical produces over 400 million lb/yr of methyl acetate by esterifying methanol with acetic acid. Reactive distillation is a promising technology to increase the efficiency and reduce the cost of this step.

In the third step, the ester undergoes hydrogenolysis to produce the desired ethanol product and recycle alcohol for the esterification step. Hydrogenolysis of esters is also a well-known, high volume industrial chemical process technology. For example, most new plants built in the last twenty years for producing 1,4-butanediol (an important monomer) use a route based on the hydrogenolysis of dimethyl maleate or a similar ester. The process scheme is illustrated in Figure 3.75.

Figure 3.75 ZeaChem Indirect Ethanol Process Block Flow Diagram



Source: ZeaChem Inc.

The net result of the indirect route for ethanol production is a 50 percent improvement in molar yield compared to conventional direct fermentation technologies. That is, 3 moles of ethanol are produced per mole of 6-carbon sugar, as contrasted with 2 moles of ethanol per mole of 6-carbon sugar by conventional ethanol fermentation. The energy for the third mol of ethanol is supplied by hydrogen. Biomass gasification is a particularly attractive path to hydrogen production since it uses energy in lignin and non-fermentable cellulose, hemicellulose, starches and sugars, which can be converted into part of the chemical energy in the ethanol product. Also, since many homoacetogens metabolize both five and six carbon sugars, the chemical energy of all of these three major biomass fractions can potentially be converted in the first step as well, and then to ethanol at high overall energy efficiency with the indirect route even if the expected conversion of dextrose in the first step is not achieved.

In April, 2005, ZeaChem completed a detailed feasibility study, based on bench scale testing of the fermentation steps and other process features, as well detailed process modeling, flowsheet development, and cost estimating. This work was sponsored by a US DOE grant (DE-FG36-03GO13010), under the Office of Industrial Technologies, Inventions, and Innovation Program. The results indicated good feasibility for further development of this technology.

3.4.4 Vertigro System

Valcent Products, Inc. and Global Green Solutions, Inc. have developed a joint venture (Vertigro Energy) which includes the growing and harvesting of algae and extraction of vegetable oil from the algae for biodiesel production. 90 percent by weight of the algae is captured carbon dioxide, which is "sequestered" by this process and so contributes significantly to the reduction of greenhouse gases. The Vertigro technology employs a proprietary high-density vertical bioreactor (constructed from plastic sheeting) that produces fast growing algae which yield large volumes of high-grade vegetable oil. Flow paths formed within the plastic sheeting allow water and algae to constantly circulate through the bioreactors. Using the natural process of photosynthesis, maximum exposure to sunlight and the absorption of carbon dioxide, the algae reproduces rapidly and continuously. Valcent has commissioned the world's first commercial-scale bioreactor pilot project at its test facility in El Paso, Texas.

Current data projects high yields of algae biomass, which will be harvested and processed into algal oil for biofuel feedstock and ingredients in food, pharmaceutical, and health and beauty products.

The Vertigro technology was developed by Valcent in recognition and response to a huge unsatisfied demand for vegetable oil feedstock by Biodiesel refiners and marketers. Algae, like all plants, require carbon dioxide, water with nutrients and sunlight for growth. The Vertigro bioreactor technology is ideal for locations adjacent to heavy producers of carbon dioxide such as coal-fired power plants, refineries or manufacturing facilities, as the absorption of CO_2 by the algae significantly reduces greenhouse gases. These reductions represent value in the form of Certified Emission Reduction credits, so-called carbon credits, in jurisdictions that are signatories to the Kyoto Protocol. Although the carbon credit market is still small, it is growing fast, valued in 2005 at $6.6 billion in the European Union and projected to increase to $77 billion if the United States accepts a similar national cap-and-trade program.

Valcent's "Vertigro" bioreactor system can be deployed on non-arable land, requires very little water due to its closed circuit process, does not incur significant labor costs, and does not employ fossil fuel burning equipment, unlike traditional food/biofuel crops, like soy and palm oil. They require large agricultural acreage, huge volumes of water and chemicals, and traditional farm equipment and labor. They are also much less productive than the Vertigro process: soybean, palm oil, and conventional pond-grown algae typically yield 48 gallons, 635 gallons and 10,000 gallons per acre per year, respectively.

3.5 FACILITY INTEGRATION

3.5.1 Overview

An integrated bio-refinery facility can produce both electric power and major chemicals or liquid fuels using high-efficiency gasification and integrated technologies and downstream processes. With high prices for oil and natural gas, this type of large-scale integrated facility may offer superior investment returns, as well as a hedge against raw material supply constraints.

3.5.2 Overall Value Premise

Advanced gasification technologies have raised the efficiency of biomass conversion far above that of conventional manufacturing processes, and offer the promise of economically and environmentally acceptable uses for biomass in the petrochemical and fuel industries. In the integrated production facility, the gasification of biomass produces synthesis gas (syngas) that can be used partly for the generation of electricity in conventional integrated gas/steam turbine combined cycle (IGCC) systems, and partly for the concurrent production of commodity chemicals or liquid fuels (bio gasoline and bio diesel). Thus, an integrated approach offers a strategy to truly maximize adding value to biomass.

This use of biomass as both a fuel and a feedstock in a technologically advanced facility represents a modern approach to maximizing biomass's potential, far beyond the way in which co-generation maximized the values of fuel in chemical facilities in the 1980s and 1990s. Thus, the concept of integrated bio-refinery offers a highly flexible, highly competitive cross-sector design and implementation with a multi-faceted value premise:

- Feedstock Flexibility

  The gasifier can operate on biomass or other hydrocarbon source feedstock, with superior environmental performance

- Peak Period Optimization

  Because the synthesis gas produced in the gasification can be shifted to/from power generation and chemicals/liquid fuels, it offers inherent peak period maximization capability for electric power and facility revenue optimization

- Economy of Scale

  Sharing facilities between power generation and chemicals/liquid fuels production provides both with improved scale and efficiency of the capital investment and operations support

- Higher Economic Potential

  This integrated facility has economic potential since the syngas produced in the gasifier can have several applications:

  - Town gas for heating, cooking, etc., depending on the location of the complex
  - Power generation via IGCC
  - Liquid fuel production: diesel or gasoline
  - Hydrogen for fuel cells
  - Derivative chemicals

- Environmentally Superiority

  Lower emissions of sulfur oxides, nitrogen oxides, and particulate matter compared to conventional manufacturing processes. The gasifier design produces CO_2 that is more concentrated and more easily collected and sequestrated.

3.6 TECHNOLOGY SUMMARY

Nexant concludes the following concerning biofuels technology:

- With the growth in the current mode of ethanol production by fermentation of grain and sugar feedstocks, comprised of corn, wheat, other major coarse cereals, sugarcane and sugar beets, dislocations are likely to occur in world food and feed markets; to avoid these, similar starch and sugar crops such as sorghum and cassava will be further developed in agriculture and processing technology

- An attractive optional solution for extending ethanol production is in using emerging technology to convert biomass wastes such as corn stover, wheat or rice straw, or sugarcane biomass (field waste and bagasse) to fermentable sugars
- The next level of options include making ethanol by fermenting sugars derived from switchgrass or higher-yield “energy cane”, implementation of which will require development of a new agriculture, including extensive new switchgrass origination systems and supply chains, and modification of the current sugarcane agricultural model; much general and specific attention is being paid to these options (e.g., in the US and Brazil)
- In the longer term, as ethanol becomes a more significant petroleum replacement, to relieve logistic constraints (whether ethanol is made from grain, sugar or biomass), industry will most likely convert it to hydrocarbon gasoline fractions in integrated facilities, or make higher alcohols such as butanol instead
- Additional longer-term options include biomass gasification to make syngas for catalytic syntheses to produce gasoline fractions or higher alcohols (so-called “biomass-to-liquids” or BTL)
- Biobutanol is already a commercial technology (ABE – *clostridium*-based fermentative co-production of acetone, butanol, and ethanol) that only needs to be re-instated and improved
- Biobutanol is most likely to be more widely commercialized by taking market share from synthetic butanol in the industrial chemical and solvent markets before it achieves market share as a fuel at lower prices
- Hydrocarbons are the components of gasoline, diesel, and jet fuel; by using synthetic biology to either alter existing microbes or build new ones, these new microbes in fermentations can be made to produce hydrocarbons that directly or through further processing yield fuels that are more compatible with the current infrastructure than alcohols or ester-based biodiesel
- Gasification can be used to convert the by-products and residues from other biofuel processes as well as from the agricultural value chain that supplies these processes and agricultural, forest products, and food processing biomass wastes in general
- The current version of biodiesel, fatty acid methyl ester (FAME), is most likely a “transition” technology, which, though it can make an attractive venture given tax incentives currently in place, ultimately cannot substitute significantly for petroleum diesel in the marketplace because of feedstock limitations orders of magnitude more severe than for ethanol
- Biodiesel made by emerging technologies to hydrocrack triglycerides (fats and oils) in refineries (i.e., NExBTL and H-Bio), has improved potential for economy of scale, more rapid development, makes biodiesel more attractive for refiners’ involvement, and integrates better with the refining and vehicle infrastructure, and will likely be adopted widely in the near term

- In the longer term, synthetic diesel from biomass (made via gasification followed by F-T conversion) is likely to be more economic than conventional biodiesel, with low feedstock costs, substantial by-product credits, and great economies of scale - but the product is also essentially as toxic and non-biodegradable as fossil resource-derived diesel fuel
- FCC technology can be used to convert biomass and other biofuels materials to hydrocarbons that are more compatible with petroleum and petrochemical operations and with conventional vehicle fueling systems
- Other technologies that use different methods of producing biofuels include technologies from Virent (Aqueous Phase Reforming), Terrabon (lime pre-treatment, organic acid hydrogenation) and Zeachem (acetic acid fermentation with hydrogenation)
- Bio-refineries will incorporate biomass conversion equipment and processes to produce fuels, power and chemicals from a biomass feedstock, utilizing the value of different components in the biomass feedstocks and intermediates

- The two largest consumers of water during the corn ethanol life cycle are water consumption in crop feedstock production and the corn ethanol production process
- Steps to reduce water requirements in ethanol production are being researched as water usage and supply are becoming growing issues in many economies
- Cellulosic ethanol from biochemical processes requires the most water with a ratio of 6:1 water to ethanol. Dry mill ethanol requires a ration of water to ethanol of somewhere between 3:1 and 4:1 and cellulosic ethanol via thermochemical routes water to ethanol ratio averages out at around 1.9:1.

Other conclusions in respect to APEC member economies include:

- Fermentation of sugar, starch and grain continues to dominate in the US as most commercial scale plants in the area employ this type of technology
- Commercial lignocellulosic ethanol soon may become a reality as several commercial scale lignocellulosic feedstock based bio-refineries are being built in the US
  - Abengoa Bioenergy Biomass, LLC (Hugoton, Kansas) – converting lignocellulosic feedstocks (corn stover, wheat straw, sorghum, switchgrass) to produce both ethanol and syngas, with 11.4 million gallons of ethanol per year. Also co-producing steam for cellulosic ethanol operations and excess steam for corn ethanol plant nearby. Estimated construction and start up in 2010 and 2012, respectively
  - Range Fuels (formerly Kergy Inc.) (Soperton, Georgia) – converting biomass (comprised of unmerchantable timber and forest residues) to produce 935 thousand gallons of ethanol and 935 thousand gallons of methanol. Using pyrolysis followed by thermal reforming of pyrolysis vapors for biomass conversion. Estimated start up is the first quarter of 2010
  - Poet (formerly Broin Companies) (Emmetsburg, Wisconsin) – converting lignocellulosic feedstocks (corn cobs and/or corn fiber) to produce 25 million

gallons of ethanol per year. Integrating the production of cellulosic ethanol into a dry corn mill process. Production is estimated to start in 2011

  - BlueFire Ethanol, Inc. (Mecca, California) – converting biomass (comprised of sorted green waste and woody waste from landfills) to produce 19 million gallons of ethanol per year. Using their concentrated acid hydrolysis technology followed by fermentation for biomass conversion. Facility will be located next to a 47MW biomass fed power plant. Project is currently delayed

- Other organizations are reported to be researching lignocellulosic-based ethanol production via fermentation routes or planning projects based on various types of biomass, including Iogen (Canada/United States), Dedini (DHR Process, Brazil), Abengoa Bioenergy (Spain), and BCI (United States)
  - Iogen is successfully operating a facility in Ottawa, Canada using their proprietary enzyme hydrolysis and fermentation techniques on wheat straw feedstock.
  - BCI is building a commercial demonstration plant in Jennings, LA, US. The unique aspect of this company's technology is the genetically modified organism based on an E. coli bacterium with the ethanol production genes of zymomonas spliced into it. The process is claimed to be ideally suited to handle biomass feedstocks that produce both C_5 and C_6 sugars upon hydrolysis
- In China, Dynamotive Energy Systems is set to support the development of a pyrolysis plant in Henan province, China. The plant will be based of the company’s fast pyrolysis technology

- Pyrolysis technology is also used in other APEC member economies such as, Canada, Malaysia and the US. In Malaysia, The Genting Group produced Malaysia’s first commercially produced bio-oil from empty palm fruit bunches

- Neste Oil has built an 800 thousand ton per year renewable diesel plant in Singapore based on its NExBTL technology. It is the largest facility worldwide for producing diesel from renewable sources including a broad variety of natural oils and fats. The new plant in Singapore will provide this APEC member economy an opportunity to develop into a center for Asian biofuel production

- A large number of other biomass gasification technologies have been proposed and are being developed worldwide, in Europe, Scandinavia, North America, Brazil, India, China, and elsewhere in Asia and in the world. Many of these are too small in scale, too weakly sponsored, are air-blown, or are so focused on power and heat production as to exclude them as candidates to commercially produce syngas for biofuels production in the mid-term

- Most APEC member economies fall in regions that do not have a problem with water resources. Member economies such as Peru and Viet Nam have physical water resources but lack the financial capability to develop infrastructure to properly distribute the water supply. Some areas of northern China and mid-west US have limited water supplies. Overall, however, APEC member economies are in a good position in terms of actual water supply resource based on a very macro economy view

Section 4 Feedstocks

4.1 INTRODUCTION

Traditional feedstocks for bio-refinery technologies such as corn and sugar cane for ethanol, and soy and palm oils for biodiesel production are now finding company in a variety of new feedstocks for bio-refineries. These include crops not traditionally grown as energy crops, plants not traditionally cultivated, as well as novel uses of materials previously regarded as waste. Non-traditional energy crops include sorghum, cassava, jatropha, and algae amongst others. Materials previously regarded as wastes include cellulosic biomass, municipal solid waste (MSW), and Publicly Owned Treatment Works (POTW) sludge amongst others. In recent years, there has been an increase in interest about non-food competing energy crops. In order to be considered non-food competing, a crop should be non-edible and should not compete for land and resources with food crops. This has significantly bolstered investment and research into conversion of feedstocks previously viewed as waste (most notably cellulosic biomass) as well as jatropha and algae.

4.2 SUGAR

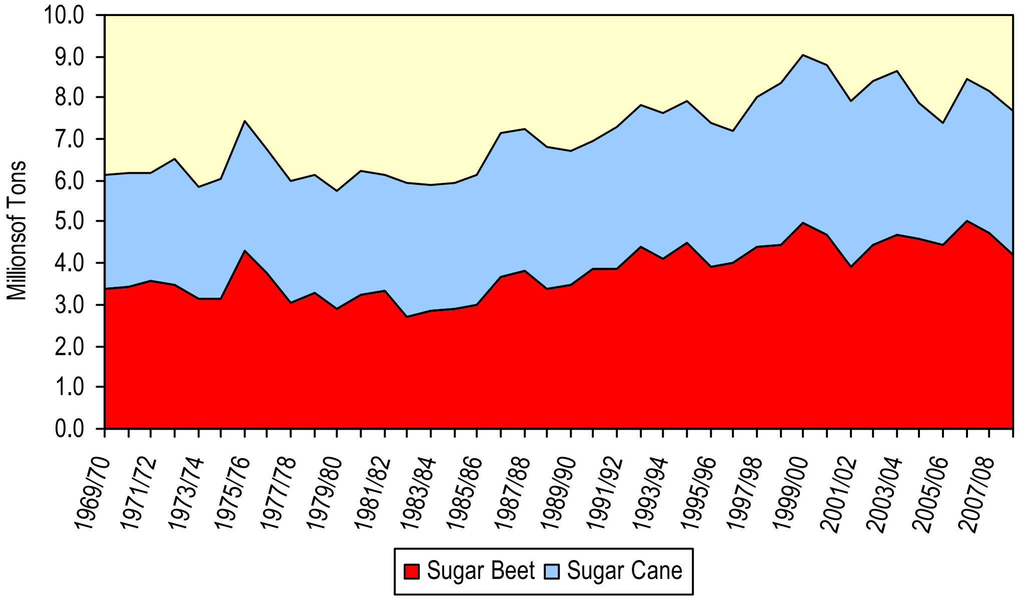
Sugarcane differs greatly in nature and commerce from corn or other grains, oils, DDGS, etc., which are traded as fungible commodities, and can be stored and shipped long distances. Typically, the cut cane with leaves removed in the field (called “dry cane” or “fresh cane”) contains 60 percent moisture and about 14 percent total sugar. In the Brazilian system, the freshly-cut cane delivered to the mill is weighed and analyzed for sugar content, and the grower is paid for the sugar content based on a formula. The formula is derived from local and international sugar market and fuel ethanol prices and other reference parameters, negotiated between growers and mill operators in a process that is monitored and enabled by the government. Note that in Brazil, 70-80 percent of the cane fields are owned by the mill, with the rest by independent growers, who have little leverage over this market relationship because they have little recourse for selling their cane. Other counties have different price-setting mechanisms. India, for example, has prices set by government guidelines, but uses more molasses, rather than fresh cane juice, for ethanol production.

Sugar prices reflect growing demands for sugar in food, but also as a substrate for ethanol production and for other growing industrial fermentation processes. Also, the price volatility and absolute price levels of sugar have been increasing in 2008. Most of the ethanol mills in Brazil, the leading producer of ethanol from sugarcane, also produce sugar. In fact, sugar and ethanol production are synergistic, in that crystal sugar production residues (centrifuge mother liquor, molasses, etc.) are sent to ethanol fermentation, and/or, assuming the facility has capacity flexibility, the two products can be hedged to respond to market conditions for both (e.g., when sugar prices are too low, the focus is on ethanol production, and visa-versa). Newer related routes to sugar-based ethanol in the future, including from sweet sorghum, by hydrolysis of lignocellulosic feeds such as energy cane, other grasses, wood, etc, will be independent of food sugar production.

Of the approximately 169 million tons of sugar that is estimated to be produced globally in the 2007/2008 year, over 80 percent is from sugarcane, and the net is primarily from sugar beets. Sugar production is expected to grow over the next decade. In the United States, sugar production volumes from beet and cane are roughly equal, with slightly more produced from sugar beets as shown in Figure 4.1. About 80 percent of annual production of cane and beet sugar is consumed domestically in the producing economies, and the net is traded. Stocks also typically run about 20 percent of annual production. Sugarcane fuel ethanol production has been studied and considered for years in the United States, but were thwarted by sugar price controls. It now appears that projects may go ahead in Florida, Louisiana, or California.

Figure 4.1 US Sugar Production from Sugar Cane and Sugar Beets

Millions of Tons



4.2.1.1 *Sugarcane*

Sugarcane efficiently turns sunlight and carbon dioxide into energy and requires a minimal amount of fertilizer, compared with other ethanol feedstocks. In rainy tropical and sub-tropical locations such as Brazil, it also can require little or no irrigation. Total input costs are less with sugarcane than with corn or some of the other crops that are used for ethanol production. The energy balance is also more positive. While corn generally produces about 1.5 units of energy for each unit of energy it consumes the energy output to input balance of sugarcane is approximately eight to one. Again, sugarcane in Brazil, India, and elsewhere is not a commodity in the same sense as grains, oils, dried cassava, etc., because it is a perishable material that degrades within hours after cutting. The leading sugarcane producing economies according to the statistics reported by the Food and Agricultural Organization (FAO) of the United Nations are shown in Table 4.1.

Table 4.1 Top Five Sugarcane Producing Economies in the World-2007

Economy	Production *(Metric tons)*
Brazil	514,079,729
India	355,520 thousand
China	106,316 thousand
Thailand	64,365,682
Pakistan	54,752 thousand

Source: FAO

Brazil has a relatively high yield of sugarcane per unit planted area. At a level of about 514 million tons per year in 2007/2008, or just over 33 percent of world production, Brazil is the largest and lowest cost producer of sugarcane, which is used for food sugar, fuel ethanol and beverage and industrial alcohol production. Together Brazil, India, China, Thailand, and Pakistan produce more than 70 percent of the sugar cane in the world. Second-tier leading sugarcane producers are Mexico (51 million tons per year in 2007), Australia (36 million tons per year), Colombia (40 million tons per year), Indonesia (25 million tons per year), the United States (28 million tons per year), and the Philippines (25 million tons per year). These, together with Brazil, account for about 80 percent of global production. Third-tier sugarcane producers include South Africa, Argentina, Guatemala, Egypt, Cuba, Peru, Venezuela, Iran, a number of smaller Caribbean islands, and other African nations.

Brazilian sugar/ethanol mills feed fresh sugar juice from cane crushing, while some other economies, such as Thailand, operate ethanol production mainly on molasses. Cut sugarcane cannot be stored, and it is generally found uneconomic in Brazil to operate on stored molasses. In Brazil, sugarcane harvesting and sugar production (and thus ethanol production) is only done only over about 200 days (7 months of the year), because the harvesting predominantly must cease during the rainy season because it is impractical and to protect the soil and plantings. Peru, which does not have this rainy season but uses irrigation from Andean rivers, has the ability to grow two crops per year. This affords Peru the ability to have the highest sugarcane yield per hectare, and may lead to Peru increasing its global market share in the coming years of both sugar and ethanol production, causing a new paradigm to emerge.

Brazilian sugarcane production is highly sustainable because irrigation is predominantly only from natural seasonal rainfall and not from fossil resources (depletable aquifers), and the practice is to return to the soil for their organic and mineral fertilizer values all liquid and solid residues from processing. However, some contrary concerns are being raised in some locations, over excess solubles (salts) leaching from these applications through the soil and into groundwater.

4.2.1.2 Sugarcane Pricing

Sugarcane has somewhat variable levels of recoverable sugar content, depending on type, growing location, season, aging before processing, and other factors. Wet, prepared cane (i.e., as typically received at the mill, without leaves and other trash) typically contains around 14 percent by weight of recoverable sugar.

Figure 4.2 illustrates the link of price setting for sugarcane in Brazil to the price of sugarcane paid to farmers. The data set above is the price paid to farmers in San Paulo State over the past eight years, in Brazilian Reals and US$ per ton of dry cane (60 percent moisture), and the data to below is the Brazilian domestic “price” (or imputed value) of a form of crude sugar (after the centrifuge in the mill) over the same period in kilograms. Note that $0.2 per kilogram is equal to $200 per ton.

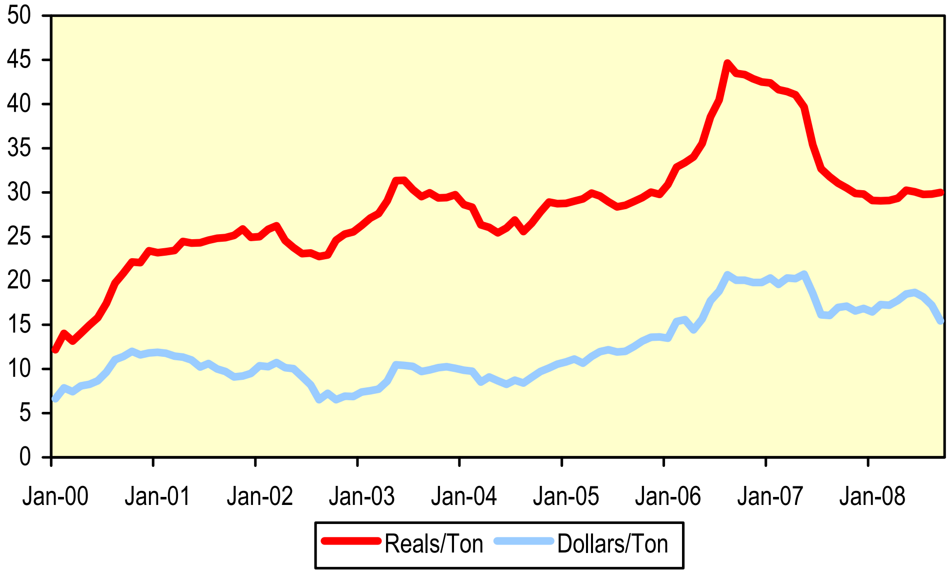
Brazilian sugarcane prices peaked at over $19 per ton (wet, as received) in 2006/2007, after several decades of being stable at levels around $8-10 per ton. In 2008, sugarcane prices settled down to around $17.5 per ton. Indian prices have been 20-30 percent higher than Brazil historically, and it is assumed that this differential will hold.

Consistent with the historical data in Figure 4.2 and Figure 4.3 a projection is presented by FAPRI (Iowa State University), of world sugar prices and world trade in sugar. This also indicates that currently, about 25 percent of world sugar production is traded and the rest is used domestically. Brazil, as well as being the largest producer, is also the largest trader of sugar.

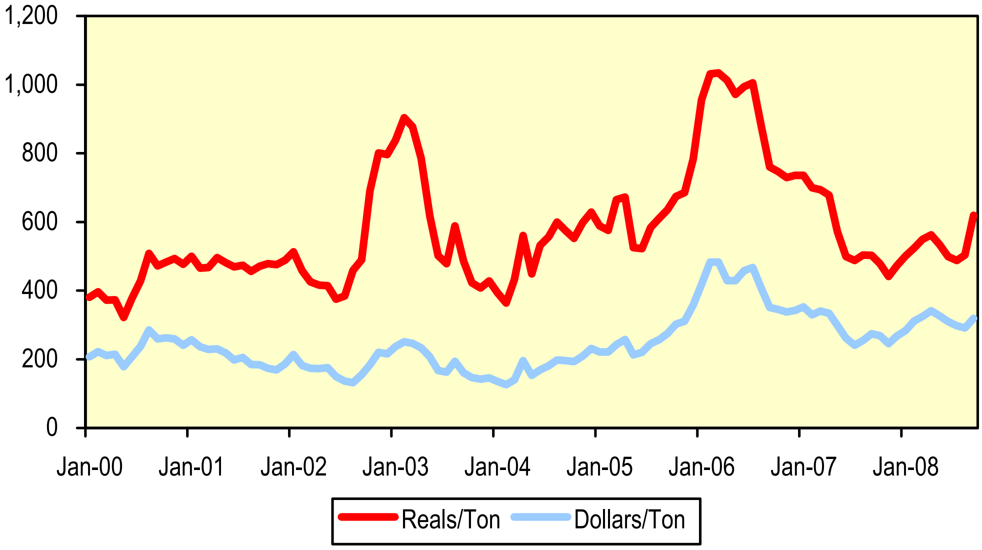
Figure 4.2 Linkage of Brazilian Sugarcane Price to Sugar Price

Sugarcane Price to Sao Paulo Farmers vs. Brazilian Domestic Market Centrifuge Sugar Prices

Sugarcane

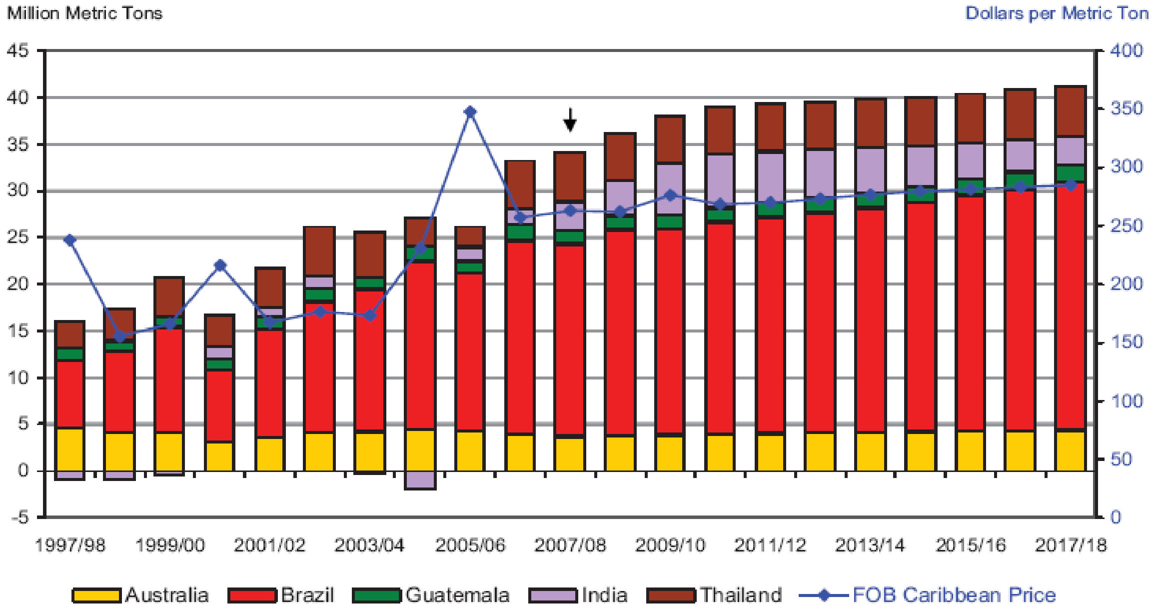


Sugar



Source: Informacoes Economicas, Sao Paulo.

Figure 4.3 Historical and Projected Net Trade and World Sugar Price



Source: Food and Agricultural Policy Research Institute, Iowa State University

Potential Major Developments in Sugarcane Sugar Yield

There has been insignificant progress in fifty years by conventional breeding to increase sugar yield from sugarcane. However, according to a September, 2006 report in Nature Biotechnology, molecular geneticist Robert Birch of the University of Queensland (UQ), Australia, introduced a bacterial gene from Pantoea dispersa, a harmless bacterial parasite on sugarcane, to encode sucrose isomerase enzyme into sugarcane. He unexpectedly found a potential to double the sugar yield. Australia has been struggling recently to bolster its sugar industry against competition from cheaper Brazilian sugar. The UQ team, with Australian 'biopharming' company Farmacule, seeks to eventually bioengineer similar yield increases in other fuel ethanol feedstock crops like sugar beets and corn, although the latter has a quite different carbohydrate regime from sugarcane. If this biotechnology were advanced and implemented globally, it would likely work to significantly reduce the world price of sugar and the cost of ethanol production from sugarcane.

4.2.1.3 Sugar Beets

The leading sugar beet producing region is the EU (91 million tons per year) including the leading producers, France, Germany, Poland, and Italy. Russia and Ukraine are next with 46 million tons per year combined production, followed by the United States (32 million tons per year), Turkey (14.8 million tons per year), and China (9 million tons per year). These account for about 78 percent of world production, followed by Iran, Japan, Morocco, and Egypt. The leading sugar beet producing economies with their production in 2007 are shown in Table 4.2 below.

Table 4.2 Top Five Sugar Beet Producing Economies in the World - 2007

Economy	Production *(Metric tons)*
France	32,338,000
United States of America	31,912,000
Russian Federation	29,000,000
Germany	26,114,000
Ukraine	16,978,000

Source: FAO

4.3 GRAINS

Grains that are currently significant as feedstocks for fuel ethanol production are led by corn (maize), and also include coarse grains (those used primarily as animal feeds and industrially – sorghum, barley, oats, and rye), and wheat. Of the coarse grains, sorghum and barley are also consumed in significant volumes. Wheat, which, like rice, is primarily used for human food and beverage alcohol production, based on culture and tradition, is a more expensive grain, but is also being used in some areas for fuel ethanol. Wheat and the coarse grains, like corn, all produce DDGS coproducts, which have value for animal feed. DDGS of all kinds are also being considered for direct use without drying as WDGS in nearby feedlot operations, or as feeds for anaerobic digestion for biomethane production to support plant operations, or for gasification to the same end.

4.3.1 Corn (Maize)

The United States is the leading producer of feed corn in the world. Global production of corn in the 2007/2008 season was 772 million tons, of which the United States produced 332 million tons, or 43 percent, and the United States provided almost 80 percent of global exports. About 65 percent of global production was used for animal feed, and the rest was for industrial production, including human food (starch, oil, and high fructose corn syrup), industrial fermentation substrate, and ethanol production for fuel, industrial solvent and reactant, and beverage end uses. Other major producers are Argentina, EU new member states, China, Ukraine, Brazil, South Africa, and Australia. China is moving from being an exporter to being an importer. Other leading exporters are Argentina, EU new member states, and the Ukraine. Current major importers are many, led by Japan with nearly a quarter of corn imports, and followed by Korea, Mexico, Chinese Taipei, the EU-15, other Latin American economies, Egypt and other Middle East economies, Malaysia, Algeria, Canada, and African economies.

Reflecting continued strong domestic demand for corn and robust exports, corn prices sharply increased during 2008 but has since declined from peak levels of $5.00-$6.00 per bushel to about $3.65 per bushel. In the United States, 56 pounds per bushel and 15 percent moisture are the standards for corn, with different standard weights per bushel and other standard parameters defined for some other grains and other commodities. The top five corn producing economies are shown in Table 4.3

Table 4.3 Top Five Corn (Maize) Producing Economies in the World - 2007

Economy	Production *(Metric tons)*
United States of America	332,092,180
China	151,970 thousand
Brazil	51,589,721
Mexico	22,500 thousand
Argentina	21,755,364

Source: FAO

4.3.2 Milo (Grain Sorghum)

Grain sorghum (also known as milo and broomcorn) is primarily grown very productively on dry land, such as in the United States Southwest and China. It should not be confused with sweet sorghum, such as is grown in Africa and the United States Southeast, which has a stalk or cane that can be crushed to produce sugar syrup.

About 65 million tons per year of sorghum grain is grown globally. About 57 percent of sorghum is used other than for feed. Less than 10 percent of United States grain ethanol production is from sorghum. China is planning some sorghum-based capacity.

In the United States, prices for sorghum tend to be about 5-10 percent higher than those for corn.

The five top grain sorghum producing economies are shown in Table 4.4.

Table 4.4 Top Five-Grain Sorghum Producing Economies in the World - 2007

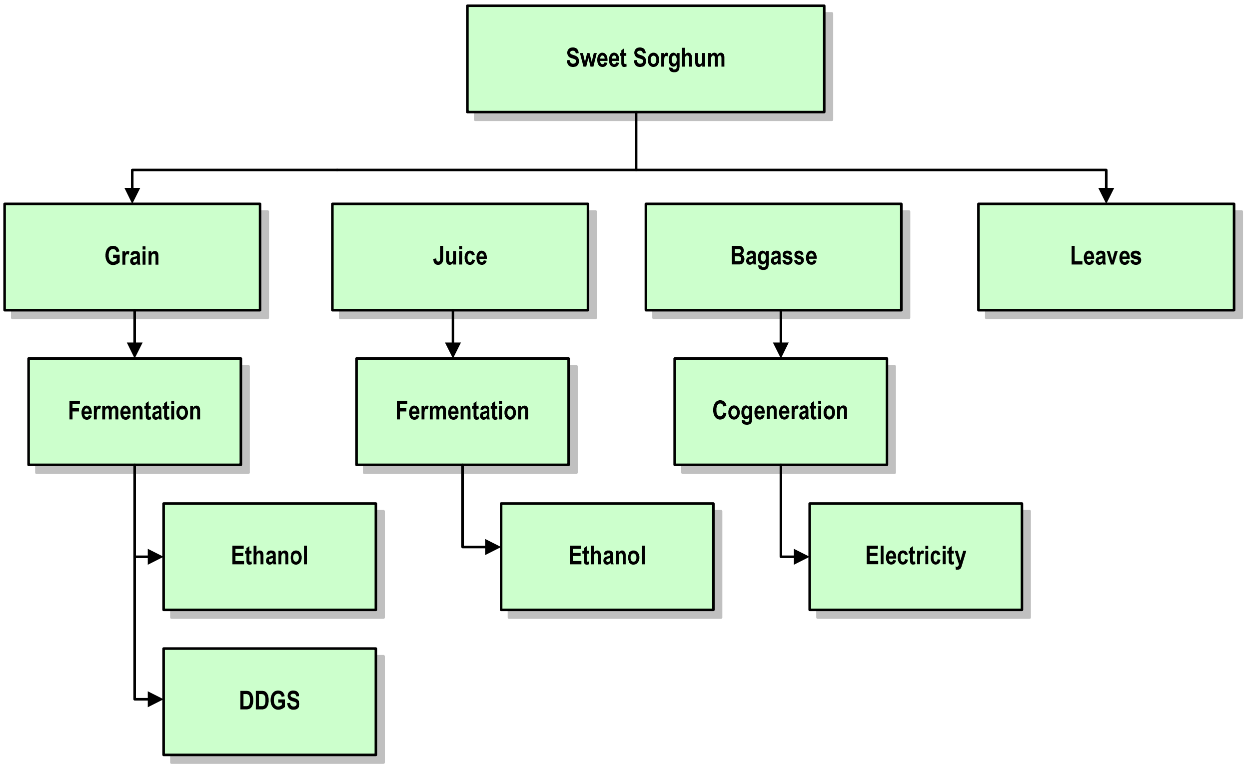
Economy	Production *(Metric tons)*
United States of America	12,827,410
Nigeria	10,500 thousand
India	7,402 thousand
Mexico	5,500 thousand
Sudan	5,048 thousand

Source: FAO

4.3.3 Sweet Sorghum

Sweet sorghum is the fastest growing source for ethanol in the world. It produces more sugar per acre than sugarcane per year. It has a higher sugar content in the juice, (14 percent for sugarcane vs 18 percent for Sweet Sorghum). It has a lower water and fertilization requirement than that of corn or sugarcane. Sweet sorghum, similar to sugarcane produces 500-700 gallons of ethanol per crop but can be re-cropped 2-3 times per year. Integrated ethanol production from sweet sorghum is shown in Figure 4.4.

Figure 4.4 Sweet Sorghum to Ethanol Production



Source: Morris Bitzer, University of Kentucky

Sweet Sorghum has attracted global attention. In India approximately 10,000 gallons of ethanol per day is made. China and India combined produced 1.7 billion gallons in 2007 from sweet sorghum. In Florida Renergie received $1.5 million in the form of a state grant to build a large sweet sorghum to ethanol facility. The UK is the main supplier of seed in world.

Sweet sorghum can be planted in rows just like sugarcane except using seed instead of cuttings. It can ratooned (cut and re-grown) at least for 3 crops and can be planted whenever the soil is above 60°F. Based on 2.5 crops of sweet sorghum per year, the biomass yield would be 400 tons per hectare per year, the ethanol yield would be 25,000 litres per hectare per year, or 6,550 gallons per hectare per year. This is about 4 times the expected yield from sugarcane.

Sweet Sorghum can be harvested with a sugarcane harvester to harvest the sugar rich stalk with a corn stillage chopper to capture the grains at the top of the stalk, as shown in Figure 4.5.

Figure 4.5 Sweet Sorghum Harvester

Source: Morris Bitzer, University of Kentucky

Sweet sorghum can be grown all over the world, but currently is mostly being grown only in India and China.

4.3.4 Wheat

Wheat is being fermented to produce fuel ethanol in Canada, Northern Europe, and the U.K., but its economics are not competitive with corn because of the high price of the feedstock. World production of all wheat in the 2007/2008 periods was about 607 million tons per year, with around 54 million tons per year in 2007/2008 in the United States, up from 51 million tons per year in 2006/2007. Wheat production has been cyclic for several decades on 5-7 year cycles, but has been trending upward, globally. In the United States, which is the fourth largest producer, wheat land is moving into corn, and yields have been low because of drought.

The other leading producers worldwide in 2007/2008, comprising over 80 percent of production together with the United States, are Europe (EU-25 plus other Europe) (91 million tons per year), China (110 million tons per year), India (75 million tons per year), Russia (49 million tons per year), Canada (20 million tons per year), Australia (13 million tons per year), Turkey (18 million tons per year), Argentina (14 million tons per year), and Ukraine (14 million tons per year). China, Europe and Russia/Ukraine are basically net self-sufficient in wheat, while North America, Argentina, Australia, and some CIS economies are exporters, and the Middle East and Asian nations are importers. Importers are not expected to use wheat for ethanol. The top five wheat producing economies in the world are shown in Table 4.5.

Table 4.5 Top Five Wheat Producing Economies in the World - 2007

Economy	Production *(Metric tons)*
China	109,860,350
India	74,890 thousand
United States of America	53,603,040
Russian Federation	49,389,860
France	33,219 thousand

Source: FAO

United States wheat prices range from about $177/ton for soft winter wheat (SWW), to about $214/ton for Dark Northern Spring (DNS). Since the United States is an exporter, these prices reflect world market prices, and are 50-100 percent higher than those for sorghum barley, rye and oats.

4.4 OTHER CROPS

4.4.1 Cassava

The cassava plant is native to South America and the West Indies. Its thick, fibrous roots, or tubers, have traditionally been processed for use in a variety of forms: bread flour, laundry starch, alcohol production, and tapioca pellets for foods. The roots contain significant levels of cyanide, which must be extracted before the tubers are further processed and used. Demand growth for cassava closely matches production, because cassava stocks are generally small in dried form, since inventory is mostly kept underground in the form of roots until needed and harvested. Figure 4.6 shows the typical recent price levels, which for dried chips are quite competitive, even perhaps at parity with those of corn and coarse grains ($160-170 per ton). Chips are the preferred feed to ethanol production.

Global cassava utilization as food, the bulk of which is in sub-Saharan Africa in the form of fresh roots and processed products, is currently at about 115 million tons per year.

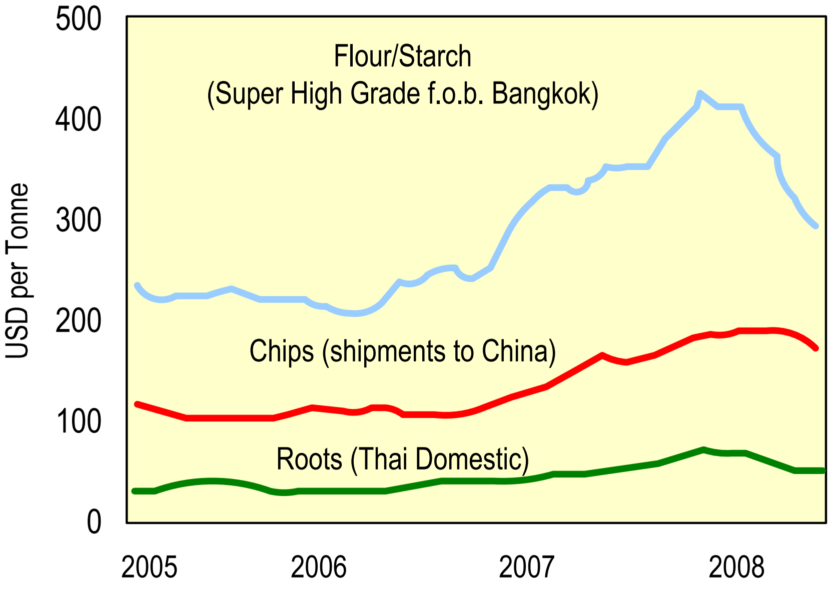
The leading producing economies with their production in 2007, according to FAO statistics, are presented in Table 4.6.

China has announced agreements or discussed intent to import cassava chips for ethanol production from markets such as Thailand, Viet Nam, West Africa (Nigeria, etc.), possibly Brazil, and elsewhere in equatorial regions.

Mimicking a measure by Brazil, Nigeria announced a policy for implementation in 2006 requiring that 10 percent cassava flour be including in the production of bread. This measure seeks to reduce the economy’s dependency on wheat imports and to provide a market outlet for cassava producers. Cassava is currently used in the form of dried chips and pellets (tapioca) as animal feed primarily in Brazil, Colombia, the Caribbean, Nigeria, China, the Netherlands, Spain, and elsewhere in Latin America, Africa, Asia, and Europe. Current forecasts are for global feed use of around 59 MM tons per year. The feed market for cassava appears to be shifting from Europe to Asia.

Figure 4.6 International Cassava Prices

United States $/ton



Source: FAO – Food Outlook, November 2008

Table 4.6 Top Five Cassava Producing Economies in the World

Economy	Production *(Metric tons)*
Nigeria	45,750 thousand
Brazil	27,312,946
Thailand	26,411,233
Indonesia	19,610,071
Congo	15 thousand

Source: FAO

Industrial applications of cassava are growing, especially in Asia, for starch and ethanol feedstock. In June of 2008, Thai Oil put on hold a cassava ethanol project, citing the feedstock costs were too high. Thai Oil has said they intend to run the plant on molasses but may consider using cassava if the prices were to drop sufficiently.

Global trade in cassava products will likely exceed 8.0 million tons (pellet equivalent) in 2008. Thailand is the world's leading exporter of cassava. Asian economies are the major importer of cassava, with China recently emerging as the leading cassava importer. A free-trade agreement has been implemented between China and Thailand, abolishing a 6 percent tariff on Thai cassava products, which has boosted their cassava trade. Though it has large supplies of grain, China's strategy appears to be to substitute imported cassava chips to preserve its corn exports and avoid imports.

4.4.2 Sweet Potato

Sweet potatoes are attracting interest for use as an ethanol feedstock, particularly in China where they are not typically viewed as a food, but also in the United States. In small scale trials, sweet potatoes grown in Maryland and Alabama have been shown to yield two to three times as much carbohydrate for fuel ethanol production as field corn grown in the same areas. In fact, the sweet potato carbohydrate yields approached the lower limits of those produced by sugarcane. It is however unclear whether sweet potatoes may be a viable alternative as biofuel source. Although they require less pesticides and fertilizer than corn, planting and harvesting incurs higher labor costs. The Chinese government, which recently put a moratorium on the use of corn for biofuels, has officially named sweet potato as a crop of preference for the production of ethanol instead. Researchers are also looking into using the crop for the production of biohydrogen. The top five sweet potato producing economies are shown below in Table 4.7.

Table 4.7 Top Five Sweet Potato Producing Economies in the World

Economy	Production *(Metric tons)*
China	102,240,110
Nigeria	3,490 thousand
Uganda	2,602 thousand
Indonesia	1,829,042
Viet Nam	1,450 thousand

Source: FAO

4.5 BIOMASS

4.5.1 Switchgrass and Other Grasses (i.e. Energy Cane)

Switchgrass has been prioritized by United States DOE program funding as a bio-energy crop of choice and was featured in the comments on the energy crisis in the last United States Presidential State of the Union Address.

Switchgrass' prospects as an energy crop highlight the potential role of genetic engineering in improving agronomic traits such as yield, mowing ease, and phased maturation (since storage against single-season harvesting is a major challenge of bio-based industry development). In Brazil, as well as eventually in the United States, there is similar interest in "energy cane", a type of cane developed by conventional breeding and/or by genetic modification. This cane grows faster, with less agronomic inputs, and with greater biomass yield at the expense of a lower sugar yield. Many entities are working on this crop as well as on switchgrass improvement. Much of the following discussion of switchgrass issues can also apply to energy cane and misanthicus. The main difference between switchgrass and misanthicus is that switchgrass may be planted with seeds, and misanthicus planted with rhizomes. This leads to an initial increase in cost for misanthicus due to higher costs of planting a rhizome than that of planting seeds, however this is made up by the fact that these are perennial plants, and misanthicus has a higher yield. For the most part, switchgrass is being championed in the United States, whereas misanthicus is being championed in Europe. Table 4.8 shows a SWOT analysis for energy grasses as a biomass feedstock for biofuel production.

Table 4.8 SWOT Analysis of Grasses as a Biomass Feedstock for Biofuel Production

	Strengths	Weaknesses	Opportunities	Threats	Additional R&D Required
Grasses (i.e., Misanthicus and Switchgrass)	Perennial Grass	Not an established crop	Potential for interesting hybrids with related grass species	Competition with other biomass crops	Improve understanding of the genetics
	High Biomass Yields	Lack of flexibility for farmers due to long term plantations			Improve the frost and drought resistance
	Non-food Crop	High establishment costs (misanthicus)			Improve productivity (yields)
	Limited Susceptibility to Disease and Pests	Limited information on genetics and other scientific areas			Improve establishment of plantations
	Low Input Crop				Test feasibility of shorter production cycles
	Fixes CO_2 in the Soil				Increase competitive ability to counter weed problems and reduce herbicide use
	Low Establishment Costs (Switchgrass)				
	Low Ash Content				
	Grows on Marginal Lands				
	Multiple Uses of Energy and Materials				
	Can be Harvested Annually for 20 Years Once Established				

Source: Adapted from EPOBIO, Crop Platforms for Cell Wall Bio-refining, April 2007

Iowa and other Heartland states are testing and promoting switchgrass cultivation, and would welcome and probably assist in funding and in other ways, switchgrass-based project development. Switchgrass is compositionally similar to corn stover for fermentation and combustion applications, and to wood for gasification, but is in many ways better. Its cultivation for combustion and gasification applications can be leveraged for fermentation projects. Switchgrass supply has many advantages, besides federal Administration support, including cost, public perception, and being unlinked from the corn harvest cycle (in contrast to corn stover). Switchgrass fermentation is on a pathway to major improvements in 5-10 years.

In the developing global system of carbon emission reduction credit trading, avoiding such emissions is beginning to have real economic value. Though the United States is not party to the Kyoto Protocols that set targets for emissions reductions to drive this market, individual companies and states are setting targets of their own. Growing switchgrass also lays down a large mass of roots that sequesters carbon for many years and may have additional value under this trading system. For this study, corn stover-based lignocellulosic fermentation is described in detail, but in the section on economics of current and future technologies, switchgrass is the model.

Byproduct energy credits proved critical to achieving viable economics for biomass fermentation. For this, it was assumed, based on previous work by others and a consensus of expert opinions, that about \$0.018/kWh would be a reasonable trading credit for CO_2 emissions reductions by using biomass rather than coal for utility power generation (related to an imputed “carbon tax” of \$50-75/ton). Another enhancement to sales to the grid of power generated from biomass is the so-called “green power price” which represents a pass through to the generator of a price premium customers can elect to pay for power generated from clean sources, including typically, hydro, wind, photovoltaics, and biomass combustion. This ranges from \$0.005/kWh to \$0.03/kWh.

Unlike corn, soybeans, and other grains, switchgrass prices are not determined by trading on any commodity exchange, so the costs of supply must be estimated based on fundamentals. Switchgrass can be grown on prime farmland, but is currently more commonly grown in Iowa and other mid-western states on cropland and pasture classified as highly erodible or marginal in agricultural productive capacity. This includes lowlands along rivers, which not only have relatively low economic value (rental or opportunity cost) but in growing switchgrass, also serve conservation purposes such as soil stabilization, wildlife habitat, etc. As such, the land is taken out of production for other crops, and is subsidized under a program called The Conservation Reserve Program (CRP). This program was initiated in 1956 as one part of the Soil Bank Act. Thus, the original CRP was commonly referred to as the "Soil Bank Program" (SB), which was designed to divert land regularly used for crop production to conservation uses under federal contracts. Farmers are generally happy with this program and are lobbying to continue to keep these lands in forest, natural meadow, or switchgrass.

Switchgrass supply for a large project has been studied and modeled by authorities of the State of Iowa, other mid-Western states, the United States DOE, and other experts and stakeholders. The general consensus is that such a supply will entail creating a system of independent, contracted growers, working with a middleman, such a grower cooperative, to deliver the required amount of switchgrass to a process plant or energy facility on a regular basis.

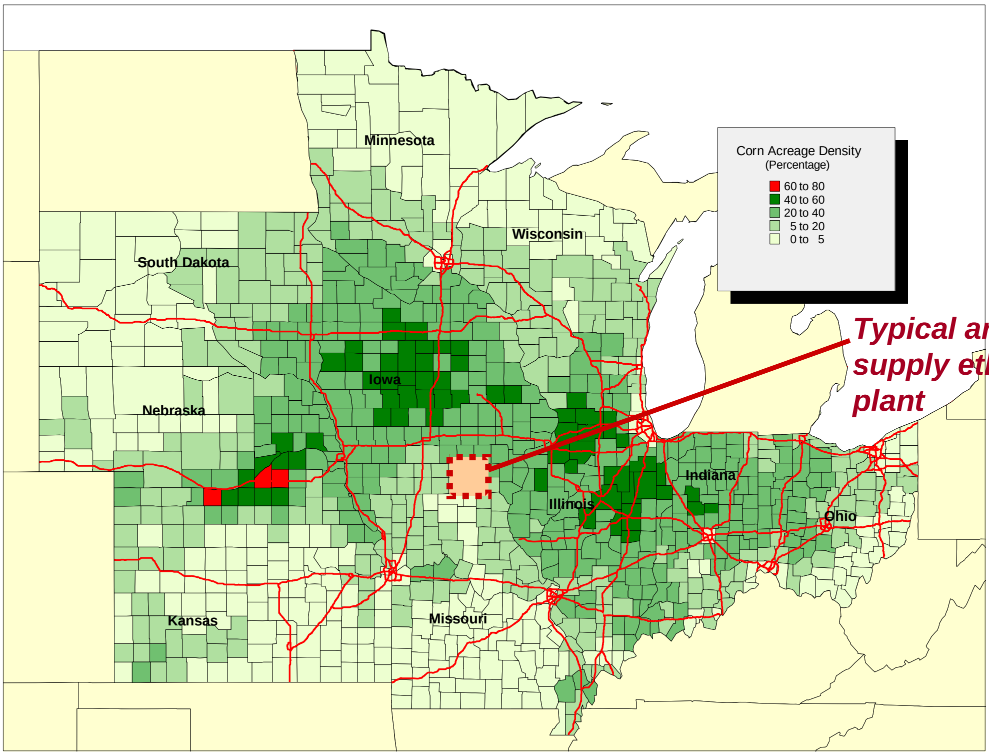
Nexant has modeled the economics of growing and supplying switchgrass. This model recognizes several logistic realities:

- Switchgrass, like any other crop, can be grown on only a fraction of the land that surrounds a central point of utilization
- The cost intensity of biomass transportation, i.e., in \$ per ton-mile, decreases with the distance of a round trip, such that the average cost of transportation of the plant’s supply is an integral of the distances and volumes supplied. So, for example, if there were a uniform pattern of land utilization within a circular perimeter of supply, half of the supply would be between two-thirds of the way to the outer perimeter and the perimeter itself
- Storage costs will become significant without development of switchgrass varieties with different maturation rates to allow staggered harvesting. Other strategies include

pelletizing or grinding and drying for storage or semi-pyrolysis (torrefaction). However, the most common storage strategy for grass-like crops today is as large bales, on the farm site

To develop a switchgrass price for this study, Nexant modeled a project area in South-eastern Iowa in the United States Midwest's corn belt, but outside the densest corn growing areas of the region, as shown in Figure 4.7.

Figure 4.7 Model Switchgrass Growing Area in United States Corn Belt



Typical area to supply ethanol plant

Source: Burton English, U of Tennessee / ORNL

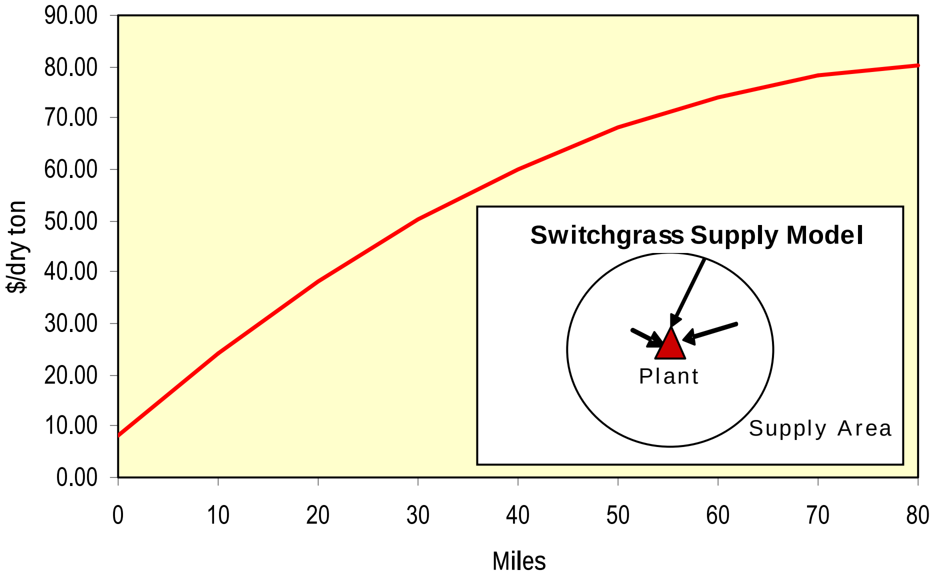
Nexant assumed a base case of 10 tons/acre yield, an 11-year growing cycle for amortization of the costs of establishing the switchgrass planting, and reseeding after 10-years. Many other analysts assumed 4 - 5 tons per acre. However, Nexant interviewed Ceres and other experts, and based on their information and projections, feels that yields of over 10 tons per acre in the near term are reasonable to assume. Based on these and other parameters developed by the USDOE, USDA, and academics working the field, Nexant has modeled the cost of producing switchgrass as shown in Table 4.9.

Table 4.9 Estimated Cost of Producing Switchgrass

	Cost per Acre *($)*	Cost per Ton *($)*
Establishment Costs		
Establishment Machinery Cost	19.90	
Operating Expenses		
Seed	24.00	
Fertilizer and Lime	60.25	
Herbicide	32.03	
Subtotal Operating Expenses	*116.28*	
Land Charges	350.00	
Total Establishment Costs	486.18	
Prorated Establishment Costs (11 yrs @ 8%)	68.10	6.81
Reseeding Costs		
Reseeding Machinery Costs	8.80	
Reseeding Operating Expenses (Seed, Fertilizer, Chemicals)	45.67	
Land Charges	350.00	
Total Reseeding Cost	404.48	
Probable Reseeding Costs (25% probability)	101.12	
Probable Reseeding Costs (10 yrs @ 8%)	15.07	1.51
Annual Production Costs		
Annual Machinery Costs	11.80	1.18
Annual Operating Expenses (Fertilizers and Chemicals)	106.78	10.68
Land Charges	350.00	35.00
Harvesting Costs		
Mowing/Conditioning	8.70	0.87
Raking/Bailing	217.13	21.71
Staging and Loading	*81.38*	8.14
Subtotal Harvesting Costs	*307.2*	
Total Annual Production Costs	858.95	85.89

Besides these agronomic costs, another important component of supplying switchgrass or any other biomass feed to fermentation is transportation and other logistics costs. The average transportation cost is determined by the yield and land utilization, which determines the required area of supply for a given plant demand. Average commodity trucking costs for the United States are $0.0535/ton-mile, but average distances are much greater than for switchgrass supplied from the field surrounding a typical plant, where the distances are likely to be 50 miles or less. That is, trucking costs per ton-mile decrease with trip distance, since loading and unloading and vehicle demurrage costs can become controlling, as shown in Figure 4.8.

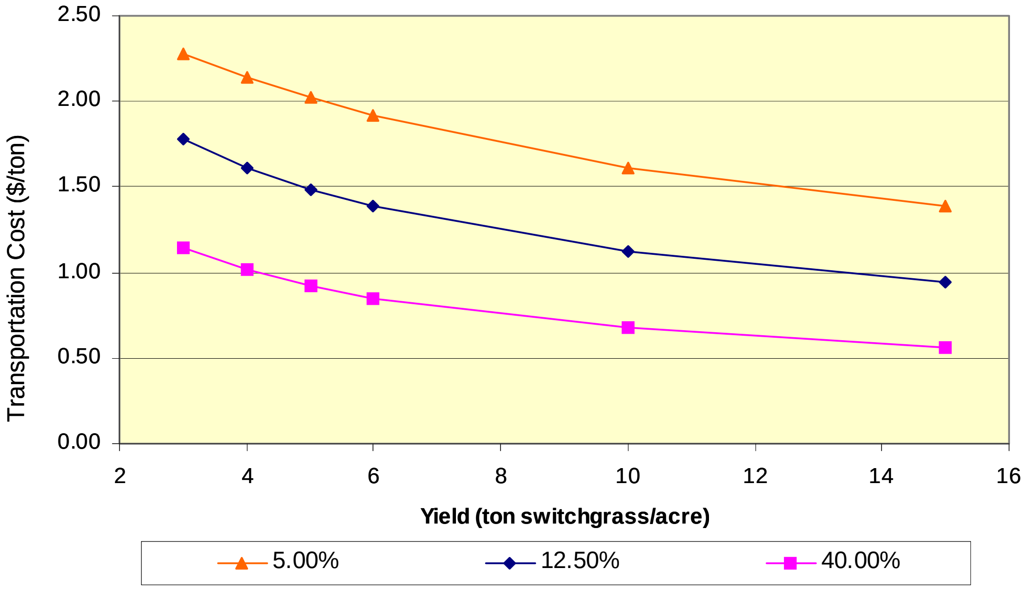
Figure 4.8 Biomass Transportation Cost Model



Source: Nexant

Experts and stakeholders have assumed among them for studies a wide range of land utilization factors up to 40 percent utilization for typical switchgrass growing. Nexant interviews with Iowa authorities indicate that they typically assume 12.5 percent utilization for examining utility switchgrass co-firing projects in the state. Ultimately, however, it was determined that switchgrass transportation costs for fermentation are relatively small compared to production costs. The analysis shown in Figure 4.9 indicates the sensitivity of biomass transportation costs to biomass yield per unit growing area and average crop growing density within the area of supply.

Figure 4.9 Switchgrass Transportation Cost Sensitivity
(the percent of land utilization)



According to the United States Congress, “the term biomass means any organic material that is available on a renewable or recurring basis, including dedicated energy crops, trees grown for energy production, wood waste and wood residues, plants (including aquatic plants, grasses, and agricultural crops), residues, fibers, animal wastes and other organic waste materials (but not including non-segregated municipal solid waste (garbage)).”(United States Congress, H. R. 1294, 2004). Corn kernel hulls, corn stover, bagasse (residues of crushed sugarcane), and rice straw, contain cellulose like switchgrass does. The cost of harvesting and transporting the residue depends on the per acre residue yield.

4.5.2 Willow and Other Trees

Vast quantities of wood wastes are available from forest thinning and from growing virgin wood resources, but the pattern of these resources are geographically and logistically so fragmented and different from switchgrass, that Nexant decided it would be inappropriate and unnecessary to include them as comparative cases. Table 4.10 shows a SWOT analysis for the use of trees as a biomass feedstock for the production of biofuels.

Table 4.10 SWOT Analysis of Trees as a Biomass Feedstock for Biofuel Production

	Strengths	Weaknesses	Opportunities	Threats	Additional R&D Required
Trees (Willow and Poplar)	Biomass Yields	Highly susceptible to rust	High demand for biofuels	Competition with other biomass crops	Improve biomass yields
	Biotechnology highly developed	Biomass yields are moderate	Breeding for high biomass yield		Improve disease resistance
	Field trials and commercial plantations of GM trees established (Poplar)	Lack of flexibility fore the farmer due to long term planations	Breeding for varieties that can be bioconverted more efficiently		Identify selectable markers for biomass/saccharification yields
	Broad genetic base	Higher cost for establishing short rotation coppice			Test feasibility of shorter harvesting cycles
	Potential for high biomass yields	Resprouting (coppicing) limited			Improve harvesting technology
	Low input crop	Farmers not familiar with the crop			Improve coppicing ability
	Non-food crop	Farmers prefer annuals			Improve drought tolerance
	Fixes CO_2 in the soil	Limited information on genetics (Willow)			
	Low ash content	High water use (Willow)			
	Easy to propagate				
	Can grow on marginal lands				
	Commercially grown in Sweden and the UK (Willow)				

Source: Adapted from EPOBIO, Crop Platforms for Cell Wall Bio-refining, April 2007

The Willow Biomass Project, one project utilizing wood biomass, is a collaborative effort by members of the Salix Consortium to grow willow and other sustainable woody crops in upstate New York. The project, funded through the United States Department of Energy's Biomass Power for Rural Development Program, seeks to commercialize willow bioenergy crops as a renewable source of biofuel. To date, the project has planted willow on at least 465 acres (1.9 km^2) of privately leased land and 25 acres of farmer-contracted land.

Willow provides a similar amount of energy per ton as other hardwoods, but can be cultivated every few years at relatively low cost. It propagates very easily from cuttings, has a quick growth cycle, and tends to re-grow following harvest. Current estimates state that it can be harvested six to seven times before it needs to be replanted. Production yields are estimated between 3.0-6.1 dry tons per acre per year.

Other trees can also be applied to this model, such as the fast growing poplar tree for example. This model can really be expanded for any tree that quickly adds biomass.

4.5.3 Agricultural Residues

Corn stover, wheat straw, and soybean hulls are residues of corn, wheat and soybean harvesting, are relatively abundant agricultural residues geographically coincident with corn (Midwest) and wheat (Plains and Northwestern states). Following a harvest, residues such as stover or wheat straw are baled, wrapped in a plastic mesh, and transported to the edge of the field. Once at the fields edge, the stover is transported to an energy facility in such a manner that 10 days of inventory are kept. However, removal of corn stover and wheat straw risks degrading soil quality and long-term productivity. Corn stover and wheat straw supply models need to consider residue levels needed for erosion control and soil carbon maintenance. Switchgrass, energy cane, and such crop residue production will compete with each other and other crops for agricultural land. As bio-energy and biomaterials production increases, demand for land for corn, wheat, soybeans and switchgrass production will increase relative to other crops. This will shift agricultural markets and land use patterns, and crop production levels and prices. The dynamics of the existing crops are more complex and more vulnerable to disruptive dynamics than switchgrass.

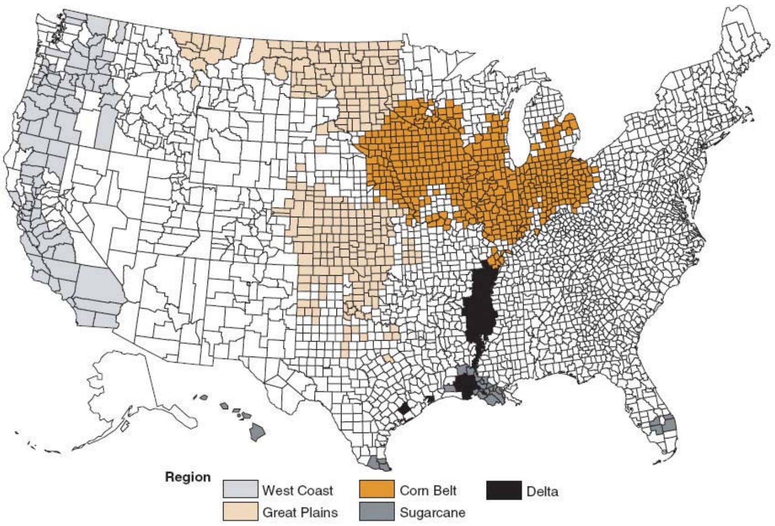
Table 4.11 lists the estimated net agricultural residue production of major producing regions in the United States, the current use of these residues for feed, and the net available to supply the energy industry. It should be realized that other technologies, such as combustion for electricity generation, or anaerobic digestion to generate biomethane for process, commercial, or utility heat and power or to supplement pipeline gas, may compete with biofuels production for some of these net resources. Figure 4.10 provides a map that defines these listed regions by county.

Table 4.11 Agricultural Residue Biomass United States and World *Supply Reduced by Animal Feeding Use*

	US Production MM TPY	World Production MM TPY	US Biomass Potential MM TPY	US Sustainable Recovery MM TPY	World Biomass Potential MM TPY	World Sustainable Recovery MM TPY
Corn	332	784	332	92.96	784	219.52
Wheat	53	607	90.1	11.13	1032	127.47
Soy Bean	70	224.6	105	n/a	337	n/a
Sugar Cane	27	1558	6.8	4	389	218
Palm Oil	n/a	43.2	n/a	n/a	65	26

Source: Adapted from – ORNL Biofuel Feedstock Assessment, February 2008 and FAO STAT

Figure 4.10 Key Biomass Producing Regions of the United States

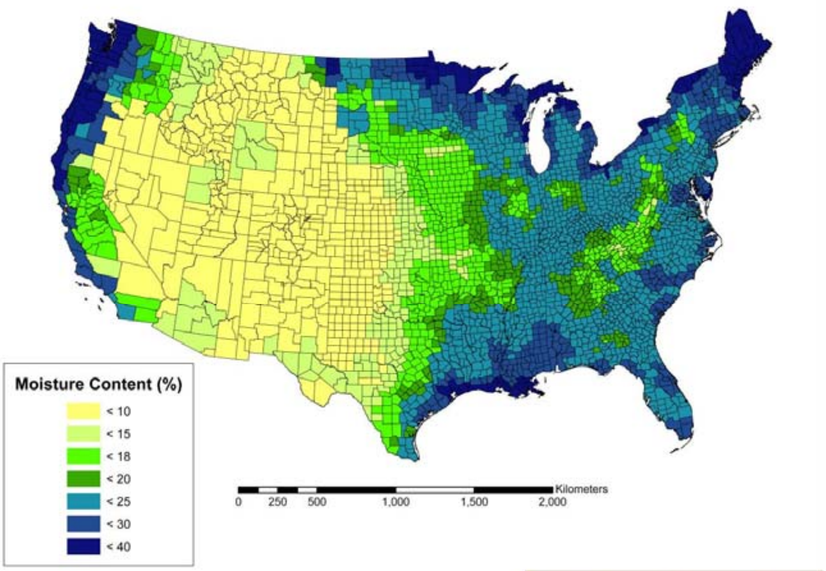


Source: ORNL

Figure 4.11 below shows the field moisture content of biomass. Moisture content is an important factor as the water weight of the biomass is a logistical hurdle. Unless the biomass is dried in the field the water is transported with the biomass, increasing costs of transport.

Figure 4.11 Estimated Field Moisture Content

Dry Basis



Data Sources: Daymet 1980-1997; AIRS 2002

Bioenergy Resources & Engineering Systems
Oak Ridge National Laboratory

Table 4.12 indicates the wide difference (2:1) among types of resources in terms of the cost of bringing agricultural residues to market use.

Table 4.12 Crop Residue Density per Growing Area

Commodity	Location	Harvest Cost	Residue Density	Transport Cost	Total Cost *(Less former payment)*
		$/MT	*MT/Sq. Mi*	*$/Ton*	
Corn Stover	Story County, IA	14	808.5	2.37	16.37
Winter Wheat	Riley County, KS	17.226	25.88	2.05	19.47
Continuous sorghum		18.26	11.23		
			Sum: 40.83		
Continuous winter wheat	Ford County, KS	23.07	23.98	~3.70	26.77
Winter wheat, fallow		32.86	41.16		36.56
Spring wheat, continuous	Norman County, MN	21.36	223.9	1.74	23.1
Barley		19.07	70.73		20.81
Oat		20.41	3.6		22.15
Rice	Arkansas County, AR	22.35	257.49	1.87	24.22

Of the 400 million tons per year of dry basis agricultural residue estimated available in the United States as in Table 4.11, some is “low hanging fruit” that is relatively inexpensive to source, while the rest is increasingly more expensive to purchase from the generators or collectors and bring to market, as greater volumes are sought.

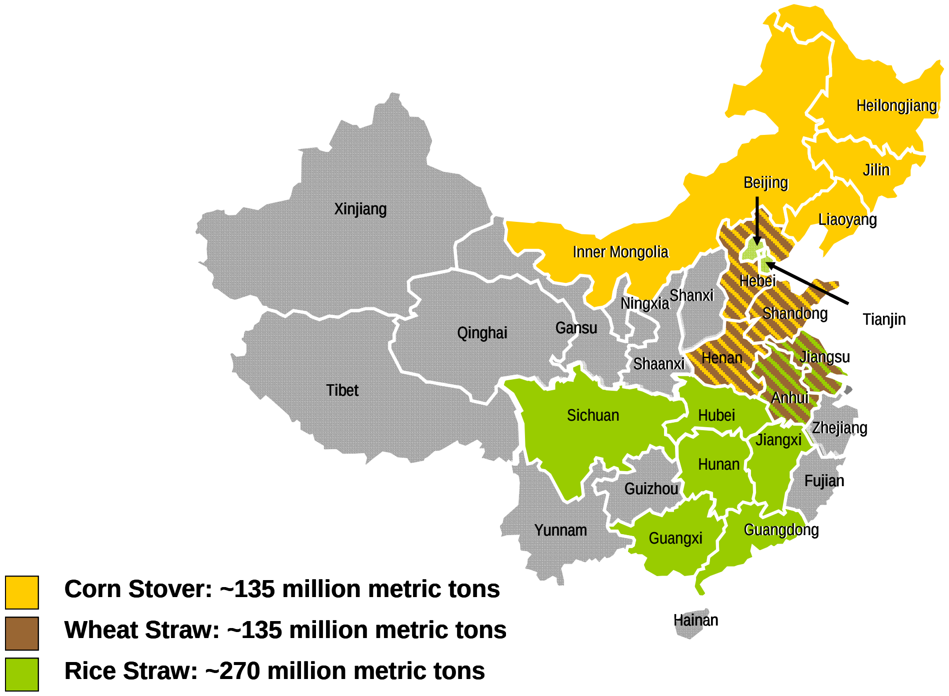
Table 4.13 shows the USDA’s estimates of the agricultural residues currently available in the United States.

Table 4.13 Agricultural Residues Currently Available – United States

Crop	Acres Harvested or Reserved	Product Yield	Residue Yield	Total Cropland Plant Mass	Harvested Product Production	Total Residue Produced	Residue Logistically Removable	Residue Sustainably Removable	Grains Used for Bioengery	Total Sustainable Biomass
	Million Acres	*Dry Ton/Acre/Year*		*Million Dry Tons per Year*						
Corngrain	68.8	3.3	3.3	450.0	225.0	225.0	90.0	74.8	16.9	91.7
Sorghum	8.6	1.4	1.4	24.8	12.4	12.4	5.0	0.0	0.5	0.5
Barley	4.3	1.2	1.8	12.8	7.7	7.7	3.1	0.8	0.3	1.2
Oats	1.9	0.8	1.7	4.8	3.2	3.2	1.3	0.2	0.0	0.2
Wheat-winter	31.3	1.1	1.9	95.4	60.1	60.1	24.0	10.0	0.0	10.0
Wheat-spring	17.5	0.9	1.2	35.5	20.1	20.1	8.0	2.6	0.0	2.6
Soybeans	73.0	1.1	1.6	193.0	115.8	115.8	46.3	0.0	0.2	0.2
Rice	3.3	2.9	4.3	23.7	14.2	14.2	5.7	5.7	0.0	5.7
Cotton lint	13.8	0.3	1.0	17.7	13.3	13.3	2.7	2.7	0.0	2.7
Alfalfa	23.8	3.0	0.0	70.6	0.0	0.0	0.0	0.0	0.0	0.0
Other Hay	39.7	1.7	0.0	67.4	0.0	0.0	0.0	0.0	0.0	0.0
Silage Corn	6.1	6.6	0.0	40.8	0.0	0.0	0.0	0.0	0.0	0.0
Silage sorghum	0.3	4.4	0.0	1.5	0.0	0.0	0.0	0.0	0.0	0.0
Other Crops	20.1	10.0	1.0	20.1	20.1	20.1	18.1	18.1	0.0	18.1
Total	312.5	38.7	19.2	1,058.1	491.9	491.9	204.2	114.9	17.9	132.9

Source: USDA Billion Ton Vision

Figure 4.12 Agricultural Residues in China



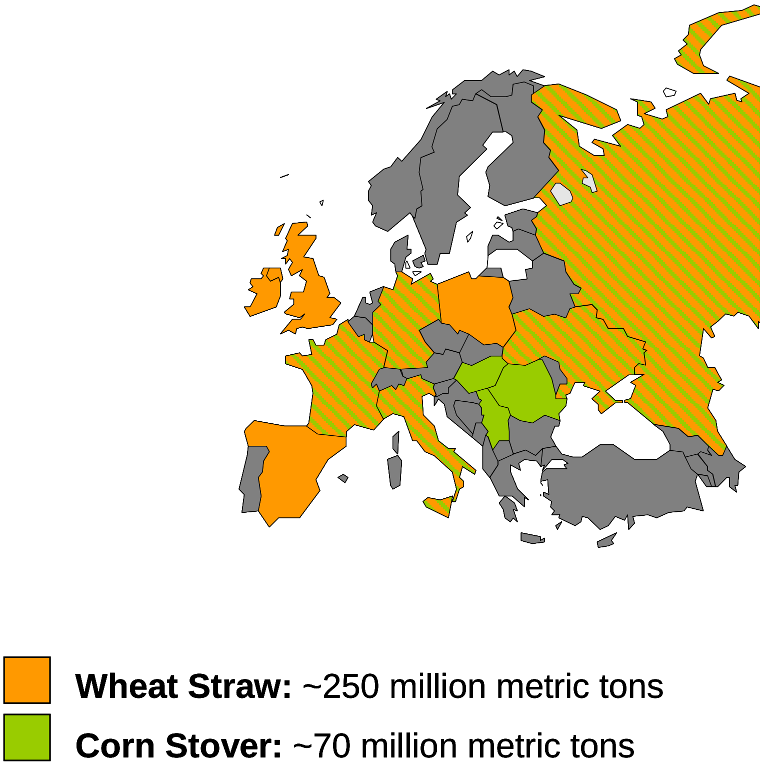
*Provinces producing more than 10 million metric tons are shown

Source: Adapted from Carsten Lauridsen, Novozymes

In China, the main agricultural crops are rice, wheat, and corn. China produces roughly 100 million tons of wheat, 135 million tons of corn, and 175 million tons of rice annually. The agricultural residues and growing regions for these crops are shown in Figure 4.12 below.

In Europe the major crop residues would be from wheat straw and corn stover. Europe produces around 190 million metric tons of wheat, and about 70 million metric tons of corn annually. Shown in Figure 4.13 are the top producing economies for wheat and corn, as well as estimates for the agricultural residues available throughout the region.

Figure 4.13 Agricultural Residues in Europe



🟧 **Wheat Straw:** ~250 million metric tons

🟩 **Corn Stover:** ~70 million metric tons

*Countries producing more than 5 million metric tons of wheat and/or 3 million metric tons of corn are shown

Source: Adapted from FAO statistics

Agricultural, forest, and consumer waste biomass has great potential as feedstock for ethanol production, but faces substantial challenges to commercialization. According to USDA-ERS, crop residues alone have the potential to displace as much as 12.5 percent of petroleum imports or generate 5 percent of the United States need for electricity. This volume may be increased in several ways:

- Increased biomass as a result of crops with improved growth
- Biomass from crops developed specifically as energy crops (e.g. switchgrass, hybrid poplar, energy cane)

- Changes in livestock feeding practices - a switch to more profitable confined animal feed operations reducing grazing land

Challenges to the creation of a successful biomass-to-ethanol industry, driving research, include:

- **Crops** - Identification of crops best suited for biomass supply
- **Incentives** - Appropriate grower incentives to encourage biomass production
- **Means** - Development of harvesting/storage/transportation systems
- **Enzyme Technology** - Pretreatment strategies to make cellulose and hemicellulose amenable to enzymatic degradation - or appropriate and economical technology to thermochemically convert biomass to a useable form of energy
- **Saccharification Enzymes** to efficiently and inexpensively convert pretreated biomass to sugars
- **Residue disposition** - to deal with unfermented residues (mostly lignin)

Biomass supplies are available from farming, forestry and municipal waste residues. While all of these feed streams represent a large volume, it is important to consider which feed streams have the best characteristics of:

- Proximity to processing
- Infrastructure concerns
- Consistency of physical characteristics of feedstock
- Supply size and stability of feedstock

A number of studies have been undertaken to address these concerns.

Table 4.14 shows a SWOT analysis of agricultural residue use as a biomass feedstock for biofuel production.

Table 4.14 SWOT Analysis of Agricultural Residue as Biomass Feedstock for Biofuel Production

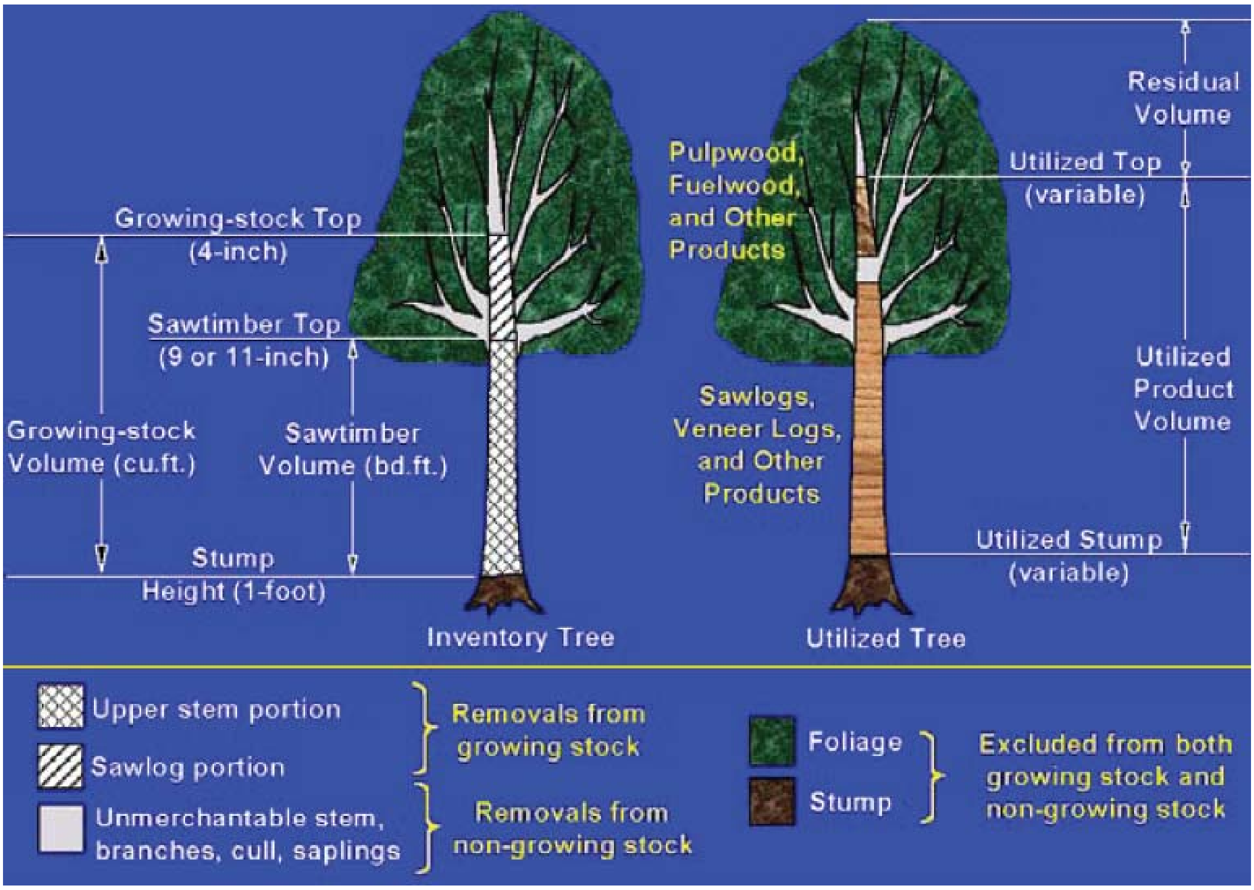
	Strengths	Weaknesses	Opportunities	Threats
Agricultural Residues (i.e., wheat straw)	Established crop	Optimization for by-product	Added value for the farmer	land competition with other food crops and biomass crops
	Broad knowledge base on wheat	Bimass yields limited	High demand for biofuels	
	Byproduct of low cost	High fertilizer input		
	Low Risk	High ash content		

Source: Adapted from EPOBIO, Crop Platforms for Cell Wall Bio-refining, April 2007

4.5.4 Forest, Paper Pulping

Typically, the trunk of the tree is used to make wood planks, and the remaining canopy is considered a "forest residue" as shown in Figure 4.14. These forest residues can be used for biomass based biofuels, such as gasification based diesel and cellulosic ethanol. In fact, wood feedstocks have been attracting a lot of attention lately from cellulosic ethanol producers. Wood feedstocks have been used as a feedstock in many of the pilot plants currently producing cellulosic ethanol in North America, and have also been used in Southeast Asia. These have been in the form of wood waste, wood chips, and even old telephone poles. Raven Biofuels in Canada is using beetle killed trees as the feedstock for their cellulosic ethanol fermentation process. Confluence Energy in Colorado is using pellets made from beetle killed trees in their process. Pacific Ethanol in Oregon is using wood chips as part of their feedstock slate. Sun Opta, Sebak, Pure Energy, Mascoma, KL Energy, and Range Fuels are all using wood chips as their feedstock of choice in multiple biofuels production processes.

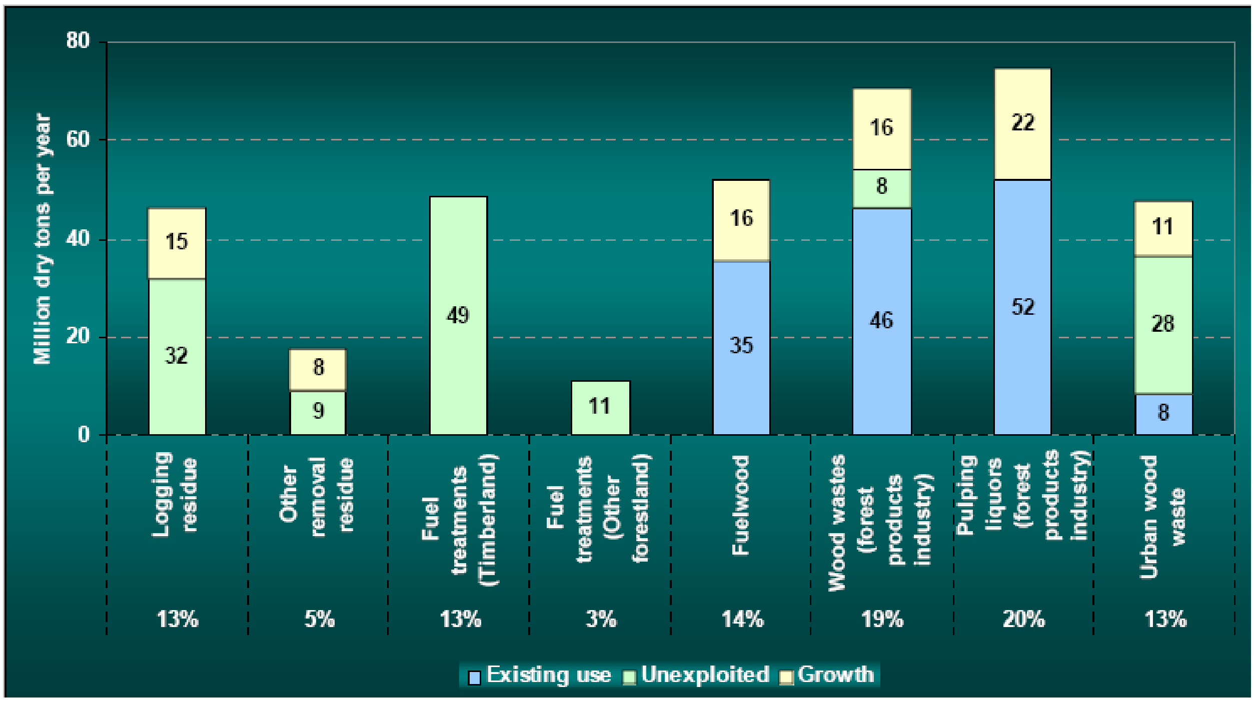
Figure 4.14 Forest Utilization



Source: USDA, Billion Ton Vision

Several paper manufacturers are also producing biofuels from wastes in their production streams, in order to make their processes more economic and to lessen energy demand. New Page is a paper manufacturer that is planning to gasify and turn the "black liquor" that is produced as a by-product of paper manufacture, into ethanol. Both New Page and Stora Enzo, which is another paper manufacturer, are both attempting to utilize the wood wastes as well from their production process in order to make renewable diesel. Figure 4.15 shows the potentially available forest residues.

Figure 4.15 Potentially Available Forest Residues



Source: USDA, Billion Ton Vision

4.5.5 Municipal Solid Waste

Municipal solid waste, or MSW, has many issues. A major distinguishing factor is the concept of "tipping fees", or being paid for taking the MSW to use as feed. However, against this are handling and storage issues with the presence of putrefiable components, the need to separate and dispose of non-organic or non-combustible components, which are potentially toxic components. MSW in the United States has the alcohol potential of 10 billion gallons per year, which is in excess of the current ethanol demand.

MSW, when in a landfill can be tapped for the landfill gas produced by the decay of organic matter. This landfill gas is a crude natural gas. Alternatively, MSW can also be processed into liquid biofuels. This can be done through gasification, fermentation, or a combination of the two.

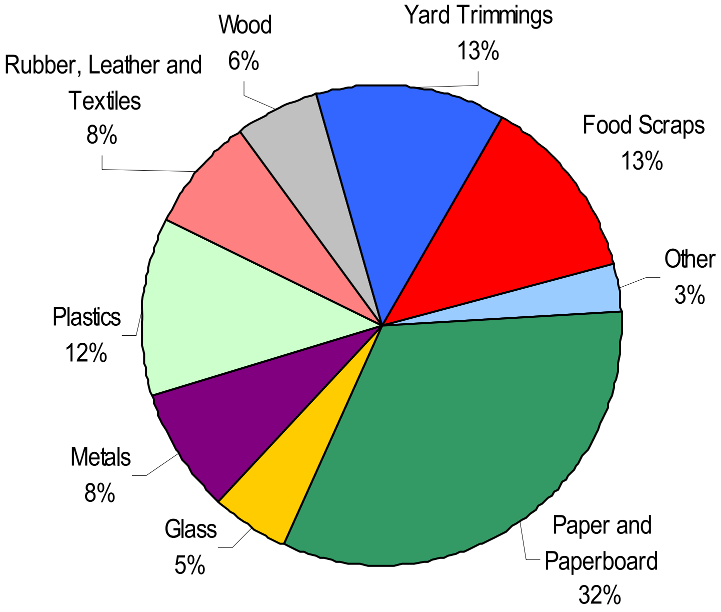
Edmonton, Alberta, will soon be home to the world's first industrial-scale facility producing biofuels from MSW. The city has signed a 25-year agreement with Canada's leading ethanol producer GreenField Ethanol Inc. and Montreal-based Enerkem, a leading biofuels technology company. The $70 million facility is slated to initially produce approximately 9.5 millions gallons of biofuel annually. Construction on the facility is expected to begin in early 2009, with methanol production starting in 2010, and ethanol production beginning in 2011.

SWANA, the Solid Waste Association of North America states, that in the United States there are, "89 waste-to-energy (WTE) facilities currently operating in 27 states, generating the equivalent of 2,500 megawatt-hours of electricity while disposing more than 29 million tons of trash". One thing that should be learned from this is that for the most part, there really is no such thing as waste anymore; one person's trash is another person's biofuel.

Figure 4.16 shows the breakdown of the different types of trash found in MSW.

Figure 4.16 Materials Generated in MSW

United States, 2007



Source: US EPA, Municipal Solid Waste in the United States 2007 Facts and Figures

Based upon this information, more than half of the MSW generated in the United States is putrefiable, and can therefore be fermented. Everything besides the metals and glass can be gasified. Table 4.15 shows the usage of MSW from 1960 to 2007.

Table 4.15 MSW Utilization 1960-2007

United States, Millions of dry tons

Activity	1960	1970	1980	1990	2000	2004	2005	2006	2007
Generation	88.1	121.1	151.6	205.2	239.1	249.8	250.4	254.2	254.1
Recovery for recycling	5.6	8.0	14.5	29.0	52.9	57.5	58.8	61.4	63.3
Recovery for composting[1]	-	-	-	4.2	16.5	20.5	20.6	20.8	21.7
Total materials recovery	5.6	8.0	14.5	33.2	69.4	78.0	79.4	82.2	85.0
Combustion with energy recovery[2]	-	0.4	2.7	29.7	33.7	31.5	31.6	31.9	31.9
Discards to landfill, other disposal[3]	82.5	112.7	134.4	142.3	136.0	140.3	139.4	140.1	137.2

[1] Compositing of yard trimmings, food scraps and other MSW organic material. Does not include backyard composting

[2] Includes combustion of MSW in mass burn or refuse-derived fuel form, and combustion with energy of source separated materials in MSW (e.g., wood pellets and tire-derived fuel).

[3] Discards after recovery minus combustion with energy recovery. Discards include combustion without energy recovery. Details may not add to totals due to rounding.

Source: US EPA, Municipal Solid Waste in the United States: 2007 Facts and Figures

Table 4.16 shows the generation and recovery of the various components of MSW.

Table 4.16 MSW Generation and Recovery by Type of Waste

United States, Millions of dry tons

Material	Weight Generated	Weight Recovered	Recovery as a Percent of Generation
Paper and paperboard	83.0	45.20	54.5%
Glass	13.6	3.22	23.7%
Metals			
Steel	15.6	5.28	33.8%
Aluminum	3.4	0.73	21.8%
Other nonferrous metals[1]	1.8	1.22	69.3%
Total Metals	20.8	7.23	34.8%
Plastics	30.7	2.09	6.8%
Rubber and leather	7.5	1.10	14.7%
Textiles	11.9	1.90	15.9%
Wood	14.2	1.32	9.3%
Other materials	4.4	1.16	26.2%
Total materials in products	186.1	63.30	34.0%
Other wastes			
Food, other[2]	31.7	0.81	2.6%
Yard trimmings	32.6	20.90	64.1%
Miscellaneous inorganic wastes	3.8	Neg.	Neg.
Total other wastes	68	21.70	31.9%
Total municipal solid waste	254.1	85.00	33.4%

4.5.6 Other Carbohydrate Wastes- Food Processing, POTW Sludge

Food Processing Wastes

Food processing wastes are gaining a lot of attention from food producers. There is a considerable amount of waste food. This seems to be supported by EnCycle, a commercial company, which aims to exploit this seam of untapped energy by converting the 17 million tons per year produced in the UK, about 30 percent comes from the food processing industry. EnCycle aims to turn some of this waste food into methane, and other products. A report by the BBC says that about a third of the food grown in the UK goes to waste. There is a real opportunity for biofuels from food waste in a developed economy like the UK where there are efficient ways of getting food from the farm to the plate, but is a real opportunity in places like India, which wastes Rupee 580 billion year because of poor post harvest facilities such as cold chains. If some of that waste could be converted into biofuels, it could go a long way to improving the lot of the rural poor. In the United States, Tyson, one of the largest poultry producers, is turning its food wastes into biofuels. Heinz, also based in the United States, has unveiled ambitious plans to reduce its greenhouse gas emissions by 20 percent by 2015 by using energy generated from potato peels. Food processing wastes offer an attractive feedstock as they can reduce energy consumption for the producer while also reducing the waste stream; however this typically seems to be a captive feedstock.

Food wastes in general are estimated to be 12.5 percent of total MSW production as shown, though that includes residential food waste generation as well.

Publicly Owned Treatment Works (POTW) Sludge

POTWs are responsible for sewer and water treatment. There is in the range of 15 million tons per year of POTW sludge produced yearly in the United States. If gasified, this can be a viable feedstock for biofuel production, typically renewable diesel. POTW sludge can be viewed essentially as biomass, however there is an issue with the amount of metals present in the sludge, and may cause issues of catalyst poisoning. Currently, a POTW basically has two options for how to deal with the sludge (without considering biofuels production). The first option is to spray the fats, oils, and greases (separated early in the treatment process) onto the dried sludge to increase the Btu content of the sludge and burn it in an incinerator. The second option is to dry the sludge and send it to a landfill. The fats, oils, and greases separated early in the treatment process, can also be a feedstock for biodiesel through transesterification to a methyl ester. However, due to the low quality and high water content, this would require a significant clean-up of the feedstock and would typically have a high free fatty acid content making traditional acid-catalyzed transesterification problematic. The East Bay Municipal Utility District (EBMUD) in the San Francisco Bay area is one POTW that is currently turning the oil that they receive (from grease trap pumpers and from waste water in general) into biodiesel and is partially running their fleet on the biodiesel produced. This has a similar benefit that MSW has in that the POTW receives a tipping fee, making the process more economical.

Since little is known about volume/composition/variability, etc. because it’s not in the interests of the waste producers or the waste haulers to track/categorize/reveal their waste stream data, there is a knowledge void in the area of POTW wastes and MSW wastes in general. Once individual waste stream has been identified and categorized, optimization of correct technology (digestion, fermentation, gasification, or pyrolysis) for specific waste stream is a fractured and diverse process. However, the solution will always be local due to the cost of transporting waste. Table 4.17 shows 2008 UN estimates for POTW sludge production in selected economies.

Table 4.17 2008 Estimated POTW Sludge Production in Selected Economies

	Estimated Sewage Sludge Production *(Dry metric tons)*
Brazil	372
China	2,966 thousand
Turkey	580
Slovakia	55
Hungary	120
Japan	2 thousand
Canada	550
Italy	1 thousand
Norway	87
Czech Republic	200
United States	6,514 thousand
Portugal	237
Germany	2 thousand
United Kingdom	1,500 thousand
Slovenia	57
Finland	150
Netherlands	1,500 thousand

Source: UN-Habitat, Global Atlas of Excreta, Wastewater Sludge, and Biosolids Management 2008

4.6 FATS, OILS, AND GREASES (FOGS)

Biodiesel, either as FAME from transesterification of natural triglycerides, or as the emerging hydrocracked natural triglyceride products such as are being introduced by Neste Oil and Petrobras, can be made from a wide range of natural gats, oils and greases. The term “fats, oils and greases”, or FOG, is often also applied to the waste greases that accumulate in public sewers and waste treatment systems, also called “brown grease”.

Virgin refined vegetable oils are the most abundant, easiest to source and most predictably priced (commoditized) type of feedstock, but also the highest priced. The main competition for these feeds comes primarily from food markets, but, to a lesser extent, also from industrial and oleochemicals uses. Next most expensive are so-called crude commodities including crude or less refined virgin vegetable oils, and rendered fats, which are co-products of animal slaughtering and processing (tallow, lard, poultry fats, and fish oils), for which the main competition is from animal feed, oleochemicals, and industrial markets. These feedstock are less commoditized (i.e., they have less formal market structures) and are less widely available geographically than vegetable oils. Tending to be even lower-priced are post-consumer waste oils such as from commercial or industrial food frying operations, called “yellow grease”. These are highly variable in quality (free fatty acids content and contamination with sludge, water, metals and unknowns are key issues), and have some established supply chains, but mostly required initiative on the part of the user to acquire supplies.

4.6.1 Virgin Oils

The major, commodity oilseeds (and in two cases, palm and olive, the associated fruits) are the source of the important vegetable oils for biodiesel production globally. The current global production of oilseeds, the degree of oilseed processing, or "crushing", and seed oil produced is shown in Table 4.18.

Table 4.18 Global Seed Oil Production by Type

2008, Million tons per year

	2008 *Million tons per year*		
Oilseed Type	Seed Production	Crushing (est.)	Oil Produced
Soybean	238.2	206.4	38.1
Rapeseed	54.1	49.6	19.4
Cottonseed	43.7	34.3	4.9
Peanut	33.4	15.2	4.9
Sunflower	32.1	28.5	11.5
Palm Oil	-	-	43.2
Palm Kernel	11.8	11.8	5.1
Copra (Coconut)	5.9	5.7	3.6
Olive	-	-	3.0
Total	419.1	351.5	133.7

Source: USDA, FAS

As seen in the table, soybean oil, rapeseed oil, and palm oil are by far the highest volume vegetable oils produced, worldwide, with sunflower oil supplies alone in the second tier, and all other oils at a much lower level. Essentially, soybean oil dominates the Americas in both volume of production as well as in use for biodiesel. Rapeseed dominates supply and is most important in Europe's biodiesel production, followed by sunflower seed oil. Palm oil is the dominant oil in Asia (primarily from Malaysia and Indonesia) for both food and planning for biodiesel, followed by soybean oil, but waste oils are also important in Asian biodiesel. Palm kernel oil has a fatty acid profile that is close to coconut oil for specialty oleochemicals markets such as personal care, so it and also high-priced olive oil are unlikely to be competitive as biodiesel feedstock. There are plans for expansion of palm oil production in Africa, elsewhere in Southeast Asia, Brazil, and elsewhere in the Americas). There is some potential for export of additional soybean oil and palm oil to Europe, and even possibly to the Americas. However, starting in 2010 palm oil imported to the European Union will have to be certified sustainable, which may cause a problem for Malaysian exports. Peanut oil has a high smoke point, useful for cooking, and is also high-priced.

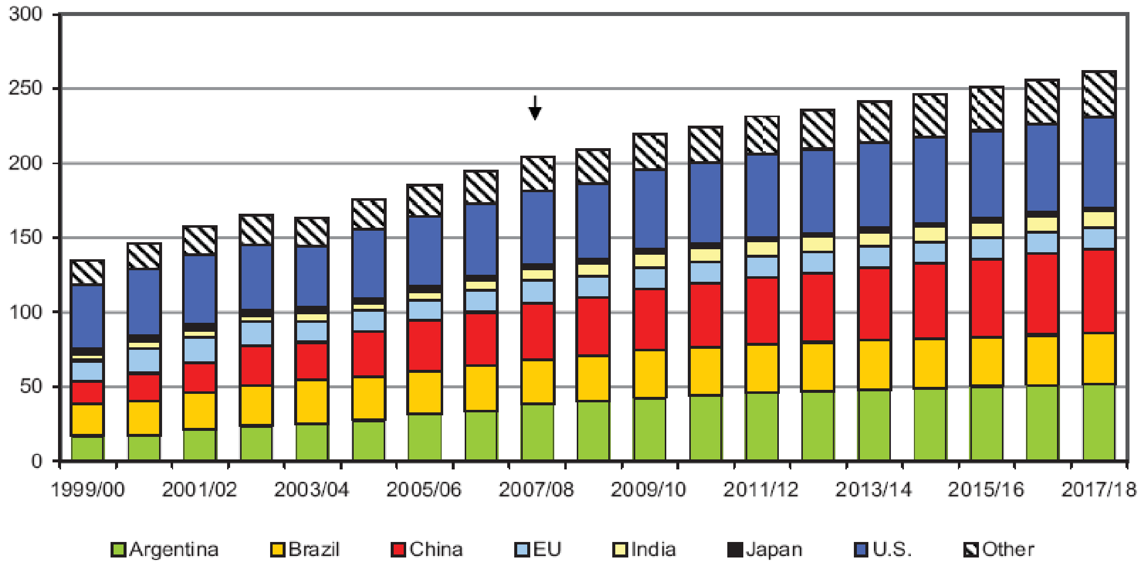
There are several other important food oils, including corn, safflower, grape seed, and sesame, which are not profiled in the table, and are so in demand for food, and so costly, that they are unlikely to be significantly used for biodiesel.

The table also shows that soybeans have a lower yield of oil than any other oil seed listed. The economics of soybean crushing depends heavily on the co-product soy meal and its market dynamics, which are discussed elsewhere in this report. In addition, the process for soybean extraction is a relatively complex one of: slicing and rolling the beans to flakes, extracting the oil with a solvent (typically hexane), separating the extracted flakes, toasting the flakes to drive off residual solvent, recovering the seed oil and recycling the solvent. This is contrasted with the expeller process, involving only some heating a mechanical squeezing of the seeds against a screen in a rotary processor. For some of the other seeds, such as sunflower, solvent steps may also be used. The extracted and toasted soy meal flakes are very dry and dusty, so to make them more palatable to cattle and other animals, they are usually conditioned to “clump them up”, by wetting with waste frying oil (“yellow grease”), or even crude co-product glycerin from biodiesel production.

Figure 4.17 and Figure 4.18 illustrate the global concentration of soybean oil production in four economies and one region (EU), specifically the United States, Brazil, Argentina, and China. Concentration in the global industry is also reflected in the fact that the major soybean producing economies are also the leading crushers, and that Europe is the biggest importer of co-product soybean meal from soybean crushing. These charts also present a view of future growth trends to the year 2017/2018. Nexant has analyzed these projections and finds them to be moderate and reasonable.

Figure 4.17 World Soybean Crush

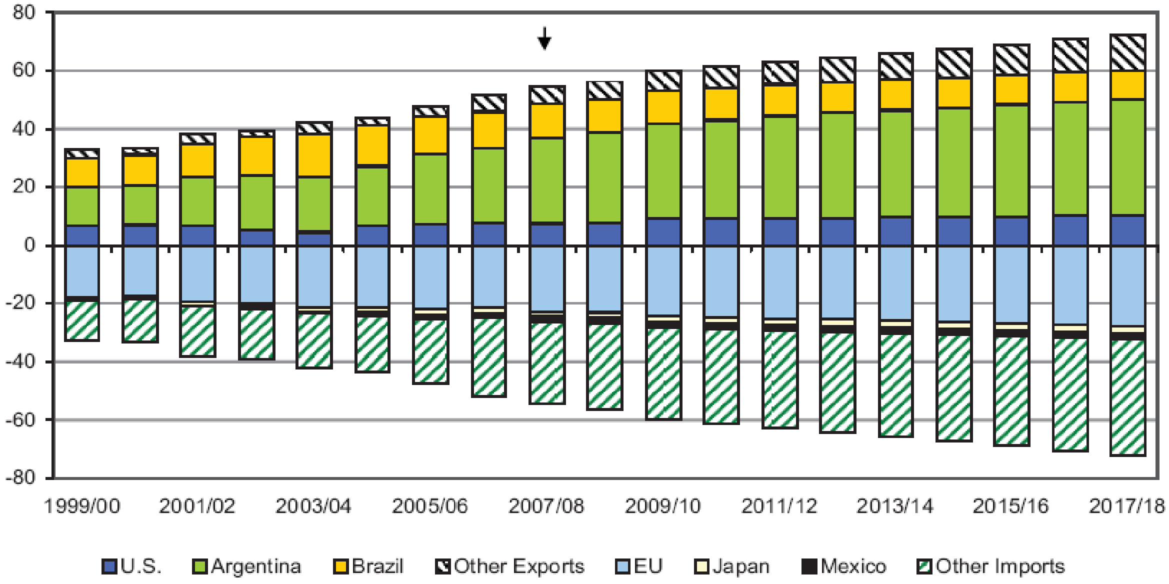
Million Metric Tons



Source: FAPRI, United States and World Agricultural Outlook, January 2008, Food and Agricultural Policy Research Institute, Iowa State University and University of Missouri-Columbia, Ames, IA, United States

Figure 4.18 World Soybean Meal Trade

Million Metric Tons

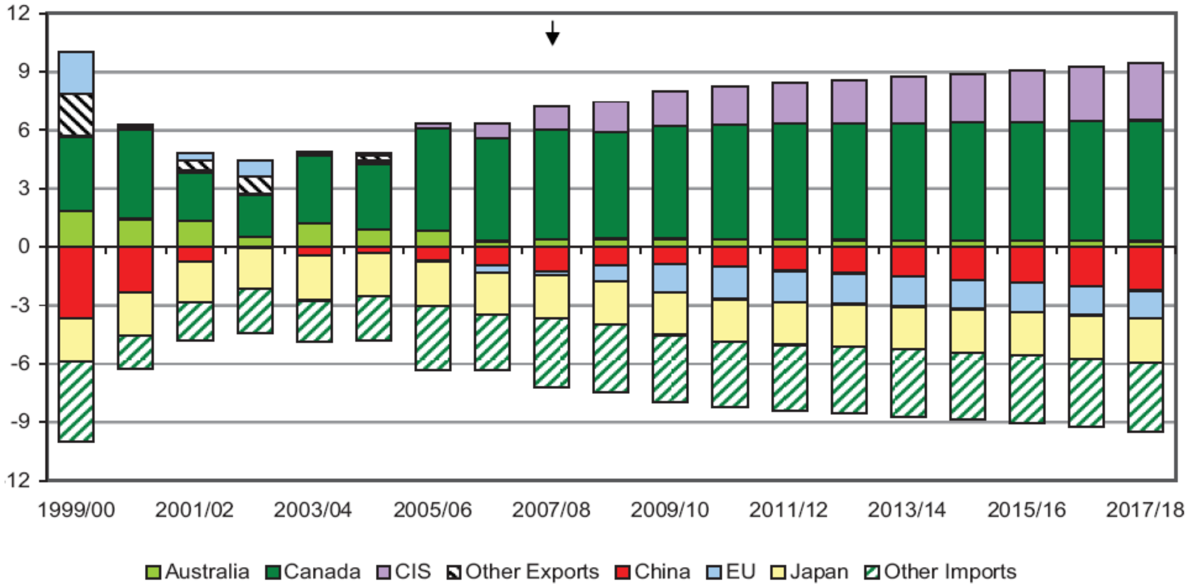


Source: FAPRI, United States and World Agricultural Outlook, January 2008, Food and Agricultural Policy Research Institute, Iowa State University and University of Missouri-Columbia, Ames, IA, United States

Figure 4.19 illustrates the degree of global trade in rapeseed, about 8 MM tons per year in 2007/2008 on a current production of about 46.4 MM tons per year, or about 15 percent. This compares with about 39 percent of soybean meal being traded. That is, while essentially all rapeseed produced is crushed for oil, this takes place primarily in the economy of origin, and the limited attractiveness of the meal limits its export potential. About 15 percent of soybeans gets used as beans and is not crushed.

The strong growth in biodiesel production in Europe, which is largely based on rapeseed crushing, is producing increasing amounts of rapeseed meal. Like soy meal, it is rich in protein and residual oil and can be used in formulated livestock feeds. It is established that rapeseed meal can replace soybean meal in dairy cow feed rations (however, 1.5 kg rapeseed meal is needed to replace 1 kg of soybean meal). In Germany and France, the industry has promoted rapeseed meal to overcome farmer resistance against its use in livestock production, stemming from earlier types of rapeseed that contained high amounts of eruric acid and glucosinolates, which caused animals to avoid the feed or resulted in digestion problems. With the new varieties of rapeseed, this is no longer the case, so farmers can use rapeseed meal in feed rations without these adverse consequences.

Figure 4.19 World Rapeseed Trade
(million metric tons)



Source: FAPRI, United States, and World Agricultural Outlook, January 2008, Food and Agricultural Policy Research Institute, Iowa State University and University of Missouri-Columbia, Ames, IA, United States

4.6.2 Crude Vegetable Oils

Vegetable oils are refined for food applications by removing many types of impurities that effect taste, odor, acidity, oxidation (rancidity) resistance, clarity, color, gumminess, etc., which might not sufficiently affect performance as a biodiesel feedstock to warrant the cost of refining. Refining steps can include degumming, refining/neutralization, bleaching, deodorization, and fractionation (including winterization) either by cryogenic or solvent-based partial crystallization.

According to the European Commission's (EC’s) latest agricultural markets report, the area devoted to growing oilseeds in the 25 European Union economies (EU-25) increased from about 5.9 million hectares in 2003 (1 hectare = 2.47 acres) to about 7.5 million hectares in 2007, with continued growth predicted. Table 4.19 shows predicted growth in terms of oilseed production and imports. Despite the projected moderate increase in oilseed production, the EU-25 will continue to import about as much oilseed as it produces, and this does not account for finished oil imports (such as of palm oil and coconut oil from Southeast Asia and elsewhere). Not all non-food uses are for fuel, since there is a large oleochemicals production in the European Union. Animal fats are also used for oleochemicals and biodiesel production. Within this pattern, use of the main feed in the European Union for biodiesel, rapeseed oil, began in 2005 to exceed its food use. This is largely driven by the European Union targeting 5.75 percent of its transport fuel needs being supplied from renewable sources by 2010, a target that cannot be met despite the current rapid rate of development.

Table 4.19 Total Oilseed Market History and Projections for the EU

(million metric tons)

	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
Usable production	17.4	19.7	20.4	24.0	23.6	28.2	28.6	29.5	30.3	31.2	32.6
of which EU-15	12.5	15.3	15.2	16.2	14.5	19.3	19.9	20.3	21.1	22.0	23.0
EU-10	4.9	4.4	5.2	5.6	5.0	4.8	4.6	5.0	5.0	5.0	5.2
EU-2				2.1	4.1	4.1	4.1	4.2	4.2	4.2	4.2
of which non-food set aside	1.8	2.8	2.6	2.3	0.0	2.8	2.9	3.3	3.4	3.4	3.5
Consumption	36.6	43.4	46.2	48.7	50.3	55.4	57.5	59.8	62.3	65.6	67.5
of which bioenergy	4.6	7.5	7.5	9.2	12.4	17.0	17.7	18.4	19.4	21.0	21.4
of which EU-15	34.2	40.1	40.1	42.0	43.7	48.8	51.0	53.2	55.8	59.0	61.0
EU-10	2.4	3.3	3.3	3.8	3.7	3.7	3.6	3.6	3.6	3.6	3.5
EU-2				2.9	2.9	2.9	2.9	3.0	3.0	3.0	3.0
Imports	20.7	24.3	26.3	28.6	27.3	28.9	30.2	31.6	33.1	35.2	35.8
Exports	1.2	0.6	0.5	2.4	0.3	0.8	0.9	0.9	0.5	0.3	0.5
Beginning stocks	7.6	8.0	8.0	8.0	9.5	9.8	10.7	11.0	11.5	12.0	12.6
Ending stocks	8.0	8.0	8.0	9.5	9.8	10.7	11.0	11.5	12.0	12.6	13.0

EU-10: Member that joined the European Union on May 1
EU-2: Bulgaria and Romania

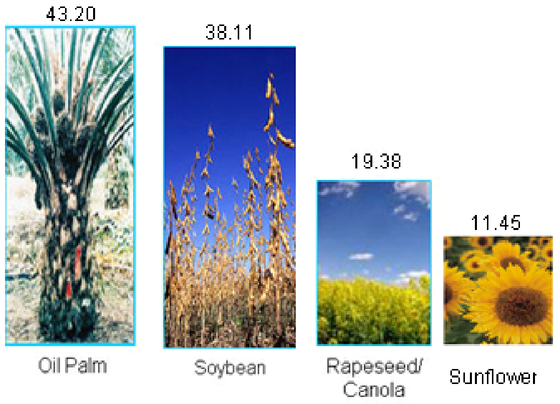
Source: "Prospects for Agricultural Markets and Income in the European Union, 2007– 2013", July 2008

Figure 4.20 indicates the global production, which is essentially equal to consumption, of five leading vegetable (seed) oils. Soybeans are largely a Western Hemisphere crop dominated by the United States and Brazil. Palm is grown in Southeast Asia, particularly in Malaysia, but increasingly in Indonesia and South America (Brazil, Colombia, etc.) and Africa. Rapeseed is grown primarily in Canada (where food varieties are known as "canola", meaning "Canada oil"), and in Northern Europe. Sunflowers are primarily a European crop, while cotton is widely grown, but processed for seed oil primarily in the United States.

Nonetheless, many lesser-known oil-bearing plants that have higher oil yields are feasible. Some of the possibilities among the most commercialized ones are listed and compared to the common sources in Table 4.20. These are typical or average yields, and individual regions, economies, or farms may have very different yields. The typical yields per unit cropland of important oilseed crops are shown.

Figure 4.20 World Vegetable Oil Production 2008/2009

(million metric tons)



Source: USDA data, adapted from a presentation by Dr. Edward Cahoon et. al.

Table 4.20 Comparative Oilseed Yields

Plant	Seed Yield *lbs/acre*	Biodiesel *gal/acre*
Corn	7,800	18
Oats	3 thousand	23
Cotton	1 thousand	35
Soybean	2 thousand	48
Mustard	1,400	61
Camelina	1,500	62
Crambe	1 thousand	65
Safflower	1,500	83
Rice	6,600	88
Sunflower	1,200	100
Peanut	2,800	113
Rapeseed	2 thousand	127
Castor bean	-	132
Jojoba bean	-	170
Coconut[1]	3,600	287
Oil palm[1]	6,251	635
Jatropha[1]	1,419	150
Micro-Algae[1]	10 thousand+	1 thousand+

[1] Yield in lbs of oil /acre

As indicated, jojoba, a minor oil crop that grows in the desert, has a very high biodiesel yield. Similarly castor beans have high yields of oil, but this oil has toxic properties that are not a liability for fuel use, but would be problematic for human contact. The Brazilian government has recently pushed castor bean biodiesel development to benefit rural economies, but has now withdrawn this initiative. The highest yielding plants, palm and coconut, are grown in the tropics. Jatropha is being heralded by the developing world as a possible biofuels panacea, as it grows on marginal lands, and is non-edible. Micro-algae, with the highest possible yields, are not yet commercially economically competitive, and serious doubts remain as to whether it can be.

On average, soybeans have a relatively low yield compared to some other feasible crops for biodiesel, but soybeans have the economic advantage (and complication) of yielding a valuable co-product from oil extraction, soy meal, which is an important component of feeds for poultry, swine and cattle as well as for other livestock and pets. It also has highly developed and efficient agronomy and product supply chains in the United States and Brazil. Besides whole soybeans serving as human and animal food, soybeans yield other foods and products such as edible oil, lecithin, soy protein, soy flour and soy hulls for fiber bran. In addition, being a nitrogen-fixing legume, it is used as a rotation crop for corn in the United States, so that many corn growers are also soybean growers. Soybeans provide nearly 70 percent of the world's protein meal consumption, with the next closest being rapeseed at 11 percent. None of the other oilseeds, except corn and perhaps peanuts have co-products with as much importance in human and animal nutrition and such other diverse economic uses. Table 4.21 profiles the world vegetable oil resources and indicates strong growth of supplies of the leading types over the last several years.

Table 4.21 Major Vegetable Oils: World Supply and Distribution
(million metric tons)

	2001/02	2002/03	2003/04	2004/05	2005/06	2006/2007	2007/2008	2008/2009
Soybean	28.88	30.46	29.88	31.86	33.47	36.32	37.5	38.11
Palm	25.44	27.28	28.78	31.56	32.97	37.34	41.29	43.2
Rapeseed	13.06	12.25	14.15	15.89	15.6	17.14	18.27	19.38
Sunflower Seed	7.48	8.17	9.15	9.03	9.69	10.6	9.99	11.45
Peanut	5.12	4.56	4.95	4.92	5.22	4.5	4.82	4.93
Palm kernel	3.12	3.30	3.56	3.83	4.05	4.45	4.81	5.1
Coconut	3.21	3.15	3.26	3.3	3.29	3.25	3.48	3.62
Olive	2.75	2.51	3.00	2.74	2.28	2.91	2.84	2.97

Source: USDA

Total palm seed oil (palm oil [PO] and palm kernel oil [PKO]) production has grown faster than soybean oil recently.

For bioethanol, though capacity is being added rapidly across Europe, it is clear that other economies can provide more competitively priced corn, wheat, and sugar for fermentation, so that bioethanol made in the European Union is unlikely to be competitive with petroleum-based fuels without government subsidies or using imported feeds. For vegetable oil-based FAME however, an earlier EC report opined that EU biodiesel could compete with crude oil at €60 per barrel (about US$77 per barrel).

Biodiesel producers often will consider the trade-offs among price, performance, and availability and choose to feed crude commodities, including crude vegetable oils or rendered animal fats such as tallow, lard, and poultry fats. Table 4.22 shows the range of prices and prices and some of the trade-off aspects of using different types of feeds.

Table 4.22 Crude Commodities for Biodiesel

(Typical pricing)

Feedstock	Price per Pound in Cents	Estimated Pounds of Feedstock per Gallon of Biodiesel	Feedstock Cost per Gallon of Biodiesel Produced
Crude Soybean Oil	$.33	7.5	$2.48
Tallow, Inedible	$.25	7.5	$1.88
Yellow Grease (<10% FFA)	$.23	8.0	$1.84
Brown Grease (>20% FFA)	$.11	8.0	$0.88

Source: The Jacobsen

Animal fats, yellow grease, and brown grease are discussed in the following sections.

4.6.3 Animal Fats

4.6.3.1 Rendered Animal Fats

Animal fats are generally rendered from animal tissues by heating to melt them and to separate them from protein and other naturally associated materials. Rendering may be accomplished by applying either dry heat or steam. Rendering and other processing of meat fats is conducted in USDA inspected plants. Over 32 million head per year of cattle, 103 million hogs, and 9 billion broiler chickens and young turkeys (the weight of broiler chickens amounting to about 16 million tons per year, for example) are currently slaughtered in the United States. There are more than 200 rendering operations in the United States and Canada, generally associated with animal slaughtering and or meatpacking. These are widely distributed among the Heartland, Southeast, Northwest, West Coast, Mountain States, Atlantic States and elsewhere where animals are processed for food.

Tallow (cattle fat) is used to produce both edible and inedible products. Edible products include margarine, cooking oil, and baking products. Inedible tallow products include soap, candles, and lubricants. Production of tallow is seasonal, and directly related to the number of cattle produced. Those economies that are the leading cattle producers are also the largest producers of tallow. The American Fats and Oils Association specifies a variety of different types of tallow and grease, including edible tallow, lard (edible), top white tallow, all beef packer tallow, extra fancy tallow, fancy tallow, bleachable fancy tallow, prime tallow, choice white grease, and yellow grease. The specifications include such parameters as the melting point, color, density, moisture content, and insoluble impurities. Similar standards are applied to rendered lard (from hogs) and poultry fats.

Table 4.23 shows the segmentation of the current volume of production and of exports of rendered fats and grease in the United States into major commercial classifications.

Table 4.23 United States Production and Exports of Rendered Fats and Greases

2007 - Thousand tons

	Production	Consumption	Export
Inedible Tallow & Greases	2,889.10	1,745.10	1,183.80
Inedible Tallow	1,675.20	341.60	809.70
Greases	1,213.90	738.90	374.10
Yellow Grease	673.60	422.80	374.10
Other Grease	540.20	308.30	
Edible Tallow	788.60	229.60	176.10
for edible use		91.40	
for inedible use		138.10	
Lard	195.70	129.20	32.90
for edible use		82.20	
for inedible use		47.00	
Poultry Fat	642.10		
Total	4,515.50	1,439.30	1,392.80

The United States supply of rendered animal fats and oils shown in the figure is estimated to be about one-quarter of the global total, which is in the order of 16 MM tons per year. This adds another 12 percent to the total supply oils, fats and greases, bringing the world total to about 149 MM tons per year today. Figure 4.21 shows the rendered FOG supply chain.

Figure 4.21 FOG Supply Chain

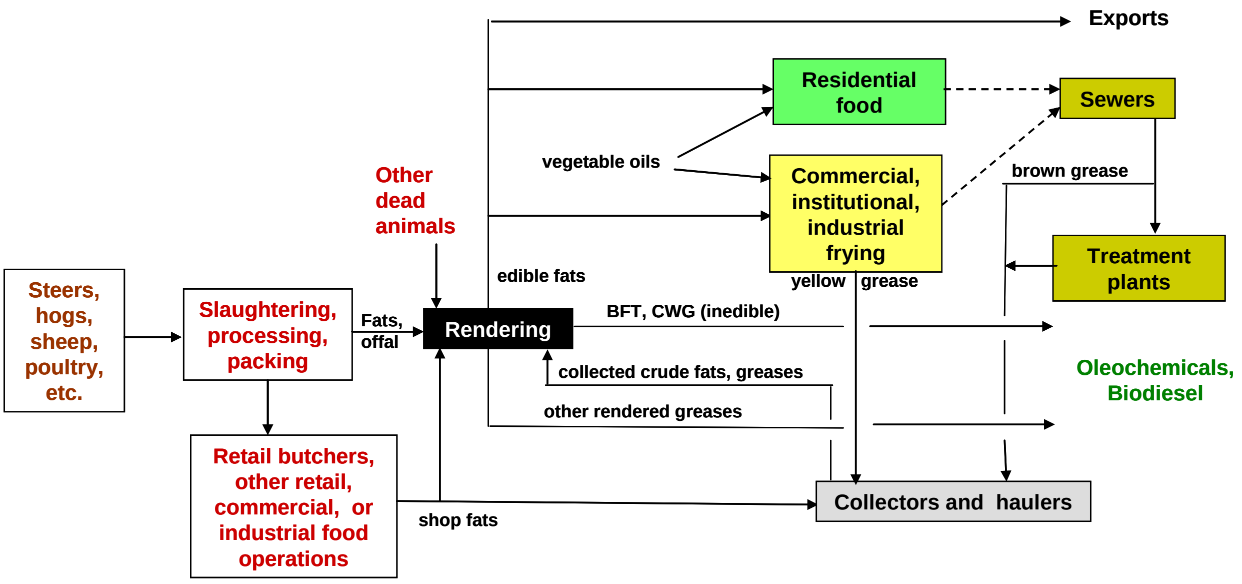
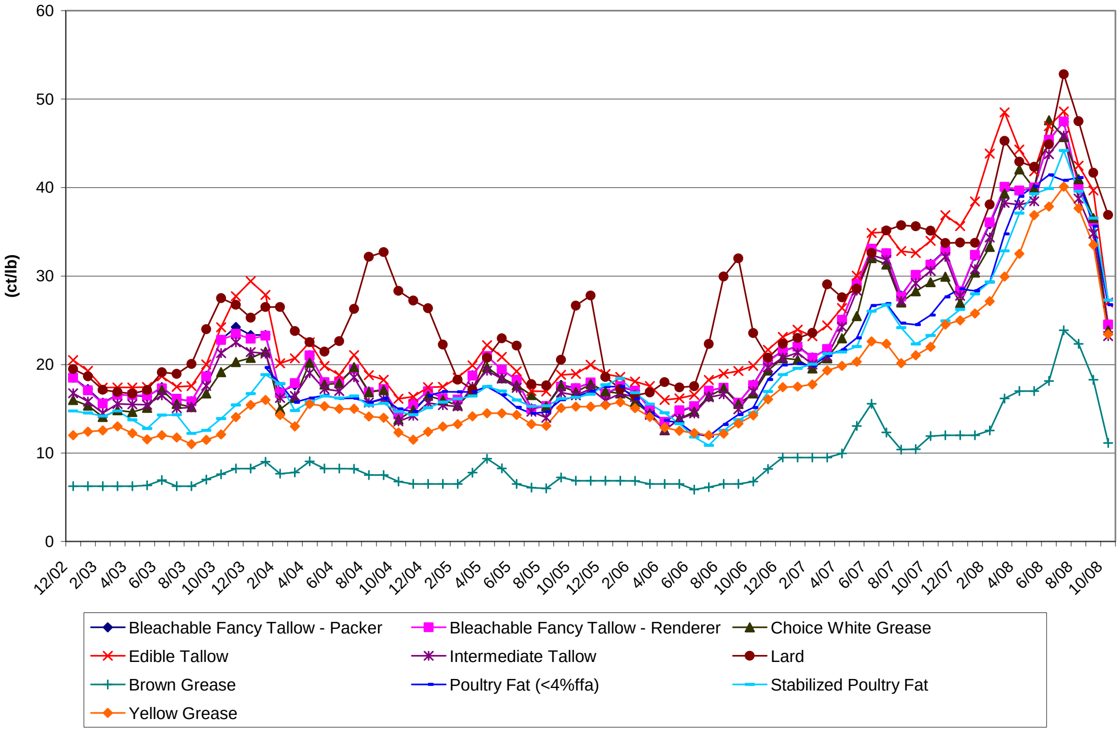


Figure 4.22 shows the prices of rendered FOGs from 2002 to the present.

Figure 4.22 Rendered Fats, Oils and Greases
(Cents per Pound)



United States prices for inedible greases typically run at $0.10-0.25 per pound, though were considerably higher in 2008 due to high prices in general.

The United States rendering industry is oriented to exporting. Approximately one-quarter of annual United States production typically is sold in overseas markets. In international markets, this trade is subject to various restrictions in different economies. Except for a complete ban of tallow by China, fats and oils import requirements by major importers of United States products remain essentially rational and based on science.

About 66 percent of inedible tallow exports go to Mexico and Turkey, and the rest to a myriad of economies around the world. Over 81 percent of yellow grease goes to Mexico, Venezuela, China, Dominican Republic, and Canada. Most edible tallow and lard exports go to Mexico.

These commodity fats are also refined in ways similar to vegetable oils. Fat rendering is currently in a complex regulatory and market relationship with the protein byproducts, bloodmeal, etc., because of concerns over transmission of BSE (Bovine Spongiform Encephalopathy, or mad cow disease) prions in human and animal contact with these products.

Animal fats generated by renderers who process non-food animals, such as "downed" livestock (those having died of disease), horses, road kill, etc. and animals or animal parts potentially infected with BSE or other related prions also can make attractively priced biodiesel feedstock.

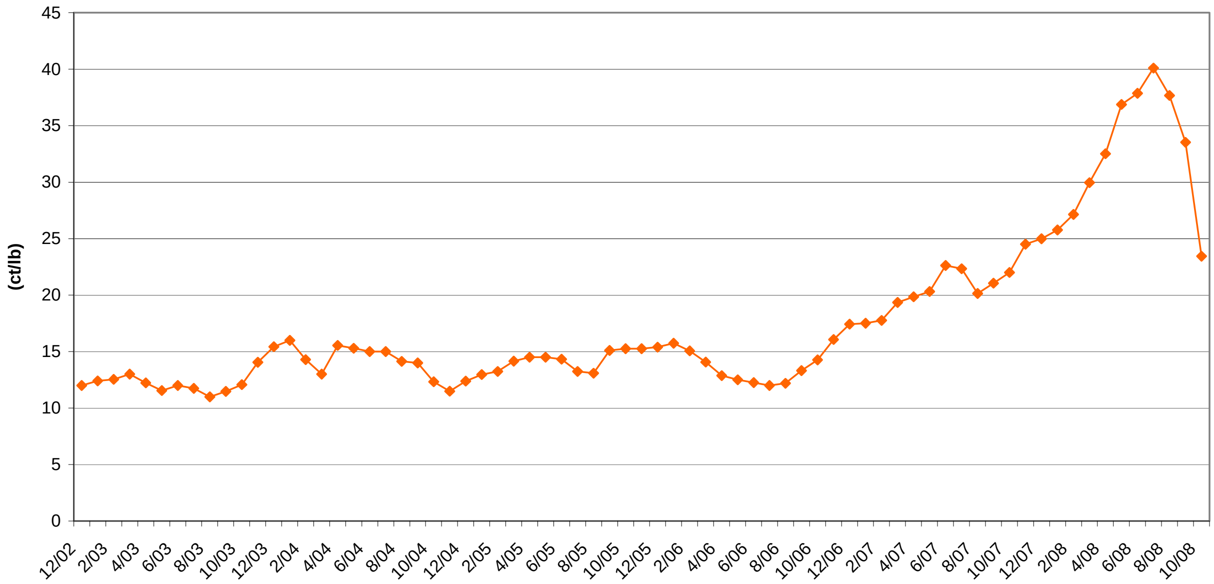
One problem possibly associated with such potentially "tainted" sources is the safety and market viability of the co-product glycerin. It may be that such glycerin would only be useful as fuel or feedstock for certain chemical synthesis, and not for refining to grades that could be used for pharmaceutical, food, feed, personal care, or other direct contact consumer uses.

4.6.3.2 Yellow Grease

Yellow grease is recycled cooking oil, and can be converted to a refined commodity by filtration and other processing similar to that used for vegetable oils for sale into animal feeding operations. It is available through collection operations from commercial food preparation operations including hotels, cruise ships, and schools, prisons, military bases and other institutions, and from bulk generators such as food processors. Restaurant chains such as McDonalds have been turning their waste "fry oil" into biodiesel in the United Kingdom. A Philadelphia biodiesel company called Fry-O-Diesel has been collecting unprocessed yellow grease and transforming it into biodiesel as well. Theme parks and amusement parks such as Disney Land, and Disney world also generate vast quantities of waste grease. Disney currently has a contract with Griffin, one of the larger renderers in the industry, for all of their waste grease. Grease haulers generally are paid by the restaurant to take their waste fry oil away, and can also be paid by the renderers for their load. Figure 4.23 shows rendered yellow grease prices from 2002 to the present.

Figure 4.23 Yellow Grease

(Cents per Pound)

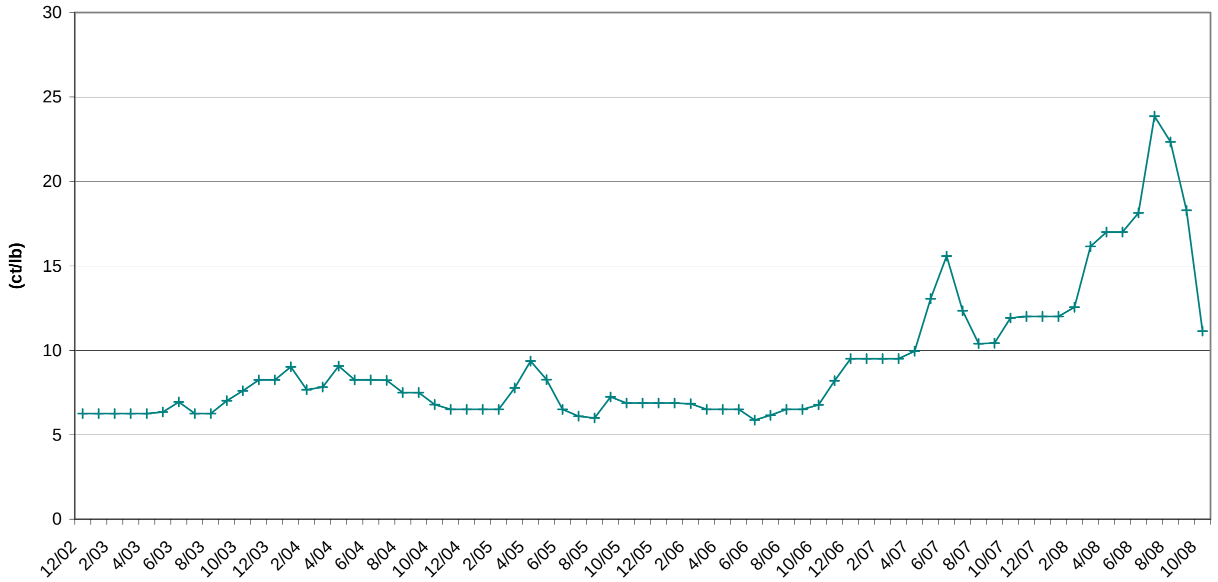


4.6.3.3 Brown Grease

Brown greases include cooking oils that have decomposed more than the norm. They may contain greases directly from the griddle, or may be composed of greases that were overcooked at renderers. In some cases, brown greases may contain trap greases from sewers. Trap greases are typically banned as animal feeds based on their source, but some blending with other greases is suspected to occur in minor amounts. It is difficult to distinguish sources of grease without extensive testing for specific contaminants such as cleaning products. Figure 4.30 shows brown grease prices from 2002 to the present.

Figure 4.24 Brown Grease

(Cents per Pound)



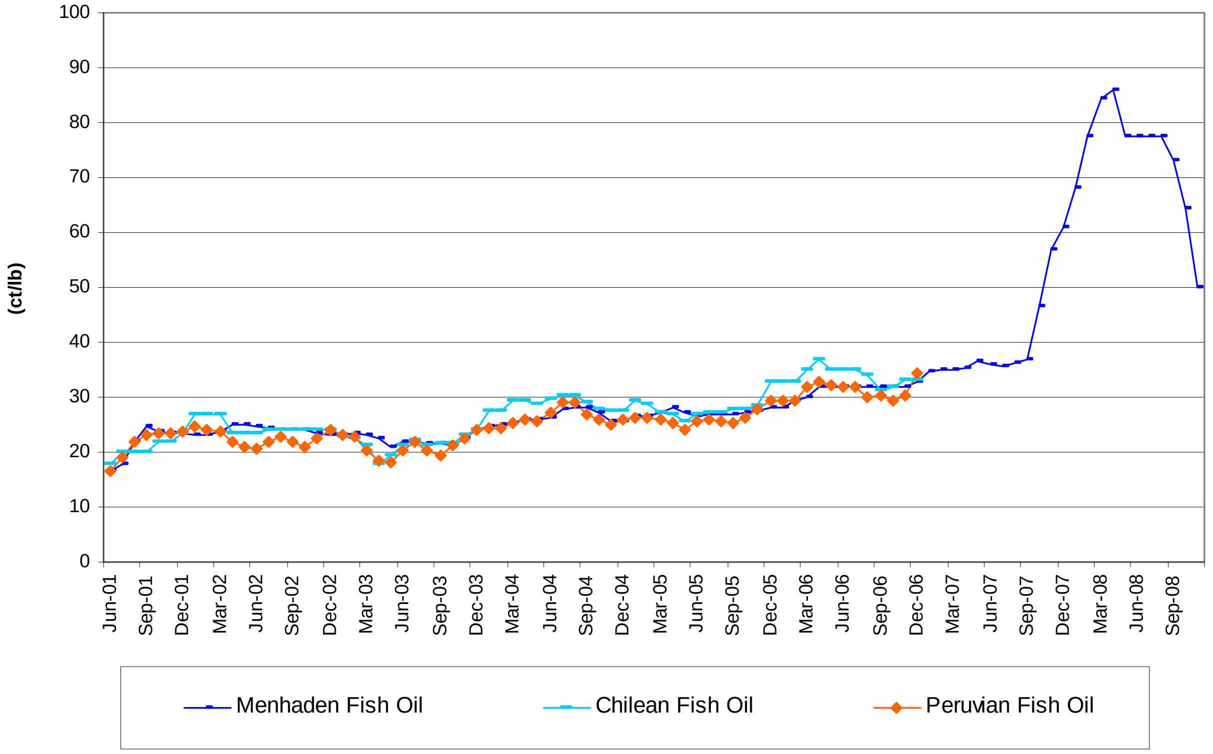
4.6.3.4 Fish Oil

World fish oil production, associated with fish meal production from whole fish reduction fisheries (i.e., processing sardines, anchovies, menhaden, herring, etc.), is typically over 1.0 MM tons per year (less than 1 percent of global vegetable oil production). Omega-3s are an important human nutritional component of fish oils that enter the human food chain directly or in feeds to aquaculture and livestock and poultry feeds. In the past, most fish oil went to direct human consumption, but this has shifted to mainly aquacultural feed use. Fishmeal producers expect that within a decade or so, aquaculture will use up to 75-80 percent of all fish oil produced.

A pilot project in Unalaska/Dutch Harbor, Alaska in conjunction with the University of Alaska Fairbanks, produces biodiesel from the fish oil by-product derived from wastes of the local fish processing industry. It is non-economic to ship this fish oil elsewhere and Alaskan communities are heavily dependent on diesel power generation. The local industry has the potential to supply about 3.5 million gallons per year (10 thousand tons per year).

Because fish oils are so valuable in aquaculture feeds, and because ocean stocks of small fish for processing are under pressure from over-fishing, it is unlikely that they will become important biodiesel feeds, except in isolated situations such as in Alaska, where they are derived from lower-nutritional and economically isolated fish processing wastes. Figure 4.25 shows Fish Oil prices from 2002 to the present.

Figure 4.25 Fish Oils
(Cents per Pound)



4.7 JATROPHA CURACS

With the current food versus fuel debate, where biofuels are blamed for food shortages and food riots- whether culpable or not, there is an increasing desire for biofuels feedstocks that do not compete with food resources. The desired feedstock should be inedible, and should not be grown on cropland that could grow food. Switchgrass and other carbohydrate energy crops fit this profile for ethanol production. For oilseeds, one feedstock that is being championed around the world, specifically in the developing world, is jatropha.

Jatropha curcas, a tropical plant with an oil rich seed, has several common names. It is known variably as the Biodiesel Tree, Pinhão manso (Brazil), Tempate (Nicaragua), Physic Nut (US), Haat (Mexico), Ratan Jyot (Hindi), Kattamanakku (Tamil), Purging Nut (Australia), Barbados Nut (Caribbean), Tuba-Tuba (Africa), as well as many others. Jatropha is originally native to the Americas, but it has become pan-tropic and is listed as a weed in Brazil, Australia, Fiji, Honduras, India, Jamaica, Panama, Puerto Rico, and Salvador. Its high oil content has been utilized for lamp oils and candles for centuries. It grows on marginal lands, preventing soil erosion. As its latex is an irritant, and the nuts are inedible, it finds use as a "living fence", used by farmers to keep livestock out of the fields. The nuts contain a toxin called curicin, which is related to the toxin ricin, from Castor seeds. A local variety is eaten after toasting, to remove the toxin, in Mexico, but this is not widespread. Jatropha is a hearty plant with characteristics similar to coffee. It is a shrub/tree that can grow to about 6 meters, although it is generally prevented from reaching this height by pruning. It usually lives 50-75 years, and grows well from seeds or cuttings though the cuttings do not grow lateral roots as long; are not as stable when they become large. Jatropha is also tolerant of steep slopes, though these would present a problem for mechanical harvesters. Frost resistant varieties exist. The tree is drought-resistant and loses its leaves during the dry season. It grows well with more than 600 mm (24 inches) of rainfall per year and cannot grow with less except in special conditions, such as Cape Verde Islands, where rainfall is only 250 mm, but the humidity of the air is very high. Although there are a plethora of jatropha species, only *Jatropha curcas* is being developed for biofuel use, largely because of familiarity. The seeds are found in the fruit; usually 3 seeds per fruit, occasionally 4. Jatropha is reported to have medicinal value as a purgative and an anti-leukemic, though the seeds are toxic. One to two seeds cause a purgative effect (vomit and diarrhea), and three to four cause death.

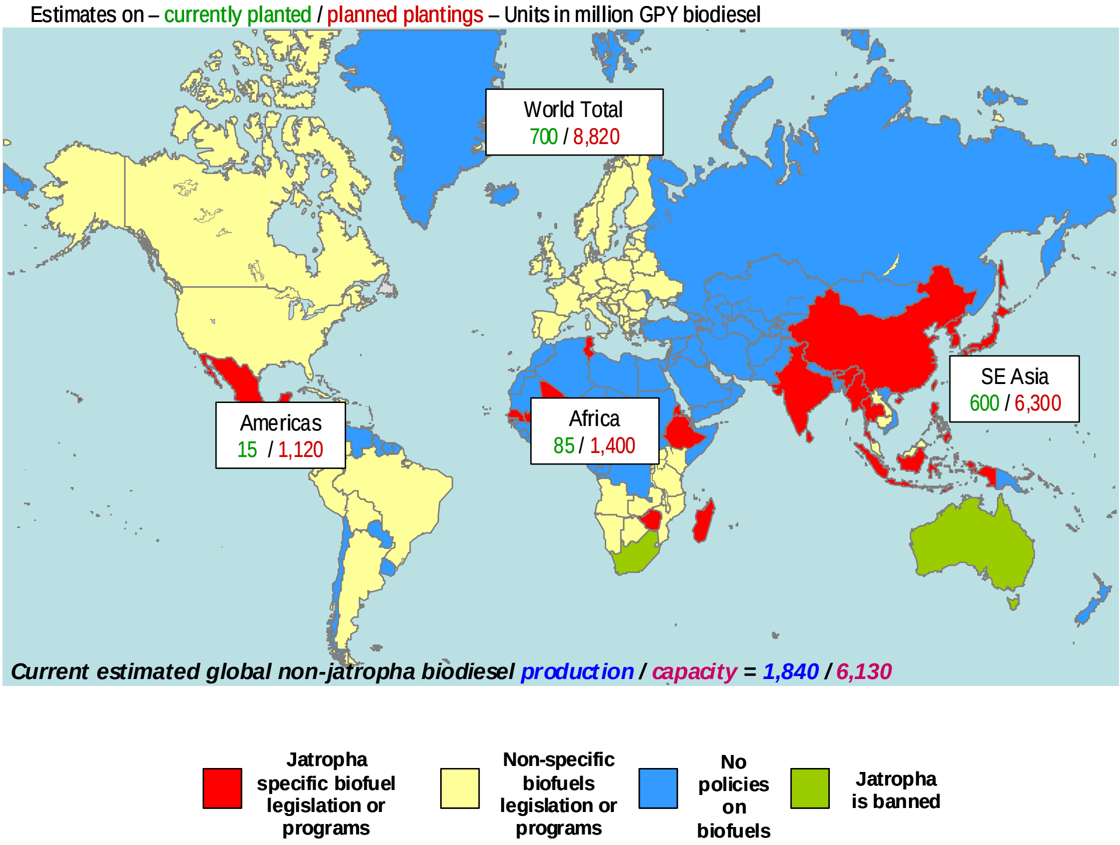
Jatropha has high oil yield and quality for biodiesel and the potential to become a world-class agricultural product, if a number of issues can be overcome. Mechanical harvesting equipment and procedures will have to prove reliable and economic. Currently this is a problem as jatropha flowers while fruiting and mechanical harvest of one batch of ripe seeds, may damage the next batch. One company in Florida, My Dream Fuel, claims its ready-for-planting trees can be mechanically harvested. Being unable to mechanically harvest jatropha is not seen as an issue in some areas of the developing world as hand harvest is done by local farmers and their families. This type of production is small scale and the crush is usually done in the center of a village, or brought to a collection location, and soap is made as a by-product. However, in order to make jatropha commercially economic in the developed world, mechanization of harvesters is a minimum requirement. Many of the other issues and concerns that have arisen over the crop in terms of agronomics, toxicity, seed harvesting, seed drying and oil extraction are well-understood and surmountable. Jatropha is currently the focus of several economies and several companies as a potential panacea for the biofuels industry, due to the high oil content, high yield per acre, and the fact that it does not compete with food. Jatropha biodiesel is very high quality as shown in the Table 4.24.

Table 4.24 Diesel and Biodiesel Specifications

		Fossil Diesel	Rape Biodiesel *(Rape Methyl Ester)*	Jatropha Biodiesel *(Jatropha Methnyl Ester)*
Characteristic				
Viscosity @ 40°C	(mm^2/s)	2.07-3.2	6	4.2
Cetane Number	(-)	43.2-52	46-54	51
Density @ 15°C	(a/cm^3)	0.815-0.859	0.882	0.879
Solidification Point	(°C)	0.9-0.24	-2	-
Flashpoint	(°C)	52-102	84	191

Figure 4.26 shows jatropha's potential to increase global biodiesel production. It should be noted that if all the announced jatropha oil production comes on line within the next decade, it will become a major oil of commerce, approaching soy oil in the number of gallons produced globally (soy oil global production was approximately 10 billion gallons in 2008). It should also be noted that whereas soy oil has other applications besides biodiesel (i.e., food products, etc.) the toxicity of jatropha eliminates these applications, leaving biodiesel, soap, and candles as end uses. Biodiesel is expected to be the major end use of jatropha.

Figure 4.26 Jatropha Production - 2008 and 2015



Americas

In the United States, JatrophaTech is developing plants and harvesting technologies in Florida. There is also biodiesel production facility planned in Chesapeake, Virginia. In addition, in Florida, My Dream Fuel has launched a campaign to recruit farmers to plant 900 thousand jatropha trees, or enough to produce as much as 1.5 million gallons of jatropha oil for biodiesel from 2,250 acres of land. The company said that its ready-for-planting trees will mature in as little as eight months, and can be mechanically harvested. In Brazil a jatropha-based biodiesel production facility with 40 thousand tons per year capacity is planned and two additional sites are being considered to make a total of 120 thousand tons year. In Tocantins, 48 thousand hectares have been planted by local farmers and 20 million hectares of degraded land can be upgraded by jatropha planting. A frost-tolerant culture of jatropha is being grown in Parana. Terasol is also promoting jatropha and distributing high yield seeds. In Argentina, 100 thousand hectares is planned by JatrophaTech. In Colombia, 100 thousand hectares is planned by a JV between Oilsource Holding Group Inc. and Abundant Biofuels Corporation. In Cuba, jatropha has historically been used for soap, but there are plans for biodiesel production from jatropha. In Mexico there is also a jatropha project planned. Jatropha is also being pursued in Honduras, Guatemala, El Salvador, Nicaragua, and the Dominican Republic. Jatropha is also found in Haiti, though not yet pursued there. In the Americas, there are more than 21 million hectares possible.

Researchers at the UC Davis are working to cultivate jatropha to grow in California. Should they be successful, this may increase the worldwide production potential of jatropha by increasing the areas in which it can grow. This research can also be adapted to climates with similar conditions to California.

Africa

Jatropha is also being championed across Africa. D1 Oils plc currently has 5 thousand hectares of managed plantations, and 30 thousand hectares of contract farming. They have also planned 20 thousand hectares in conjunction with Swaziland Government. They have 174 thousand hectares in Zambia and an off-take agreement for oil produced by Setia Group China from 28 thousand hectares in Egypt. They have 5 thousand hectares near Luxor and 500 thousand planned. The Anuanom Industrial Project Limited in Ghana currently has 2 thousand hectares and has planned 250 thousand hectares. KwaZulu-Natal has planted 4 thousand hectares, and Madagascar has planned 500 thousand hectares. In Kenya, 50 thousand hectares planned by JatrophaTech. There is also an additional 10-20 thousand hectares spread over each Zimbabwe, Mozambique Tanzania and other African economies. The African total is currently 575 thousand hectares, with 1.1 million hectares planned.

India

In India, jatropha is being developed with public and private sponsorship. D1 Oils plc distributing high yield seeds and have 44,101 hectares currently planted, 100 thousand hectares planned, with a goal of 267 thousand hectares. BP has planted 8 thousand hectares with the plan to make 9 million liters per year. The Andhra Pradesh Government has 610 thousand hectares currently, and 728 thousand hectares of wasteland cultivatable for jatropha. Jatropha plantations totaling 1.5-2 million hectares are planned. The Chhattisgarh Government has planted 20 thousand hectares, and is working with NGO’s for up to 500 hectares. In Tamil Nadu, 1 thousand hectares are planned. The Haryana Government has 20 thousand hectares planned. India currently has 675 thousand hectares planted, 2 thousand + hectares planned, and roughly 11 million hectares earmarked for jatropha. Figure 4.27 shows suitable growing regions for jatropha in India.

Figure 4.27 Suitable Growing Regions for Jatropha in India

China

China is aiming to produce 12 million tons of biodiesel annually by 2020. In Yunnan, there is 40 thousand hectares currently planted, and 1,700 thousand hectares planned by the Government, 800 thousand hectares is planned by the Shenyu New Energy Company, 28 thousand hectares by Setia Group off-take agreement with D1, a CNPC Biodiesel Production facility with a capacity of 30 thousand tons per year, and 25 thousand hectares of plantation. In Hainan CNOOC has planted 7 thousand hectares and constructed a 60 thousand ton per year biodiesel plant. In Sichuan, Sinopec has planned a 100 thousand ton per year biodiesel plant in Panzhihua with 40 thousand hectares of plantation while CNOOC has also planned a 100 thousand tons per year biodiesel plant in west Panzhihua with a plantation of 35 thousand hectares. The Panzhihua government plans to plant 480 thousand hectares and install several 10 thousand tons per year biodiesel production facilities. CNPC has also planted 120 thousand hectares. In Gungxi, D1 Oils has planned a biofuels plant that will be 10 thousand tons per year initially, and will have a 100 thousand ton expansion in the next 5 years. In Shandong, CNPC will have a biodiesel production facility with a capacity of 30 thousand tons per year and an agreement with government for feedstock. Jatropha has been grown in China since the 1980s. It has been mainly distributed in the hot-dry valley areas in Yunnan, Sichuan, Guangxi, Guangdong, and Hainan. China is Planning 12 million hectares (an area roughly the size of England) by 2010, with 2 million hectares already cultivated.

Southeast Asia

In the Philippines, 700 thousand hectares are to be planted by 2010; expandable to 2 million, along with 4 biodiesel production plants to be built. In Myanmar (Burma), 250 thousand hectares are currently planted with 2,800 thousand hectares planned. In Borneo, 200 thousand hectares are planned by JatrophaTech. Cambodia is growing 20 thousand hectares, while Viet Nam is growing 10 thousand hectares. In Indonesia, 25 thousand hectares is growing on island of Seram and 9 thousand hectares more are planned. In Laos, 9 thousand hectares are planned as well. The Southeast Asian Total is currently 300 thousand hectares, with 22 thousand + hectares planned.

4.8 OTHER NON-FOOD OIL ENERGY CROPS

Another plant from India getting a lot of attention from the biofuels industry is *Pongamia pinnata*. Pongamia has, similar to jatropha, inedible fruits. Pongamia is a deciduous tree that grows to about 15-25 meters in height with a large canopy that spreads equally wide. Oil from Pongamia seeds have been found to be useful in diesel generators and are being explored in hundreds of projects throughout India and the third world as feedstock for biodiesel. Pongamia starts yielding from 4-7 years and seed yield varies from 10-250 kg per tree. Similar to jatropha, the seeds have a high oil content of 30-40 percent, but lower phosphorous levels than jatropha, requiring less degumming. Pongamia is a nitrogen-fixing tree, and thus the seed cake has high levels of nitrogen, making it a good fertilizer. It also grows in similar conditions to jatropha. USAID recently gave a $100 thousand grant for the feasibility of Pongamia as a biofuel source. Pongamia has also received attention from Figi, where a biodiesel initiative is proposed for Fiji which will take three years for completion. This proposal by Bio-Fuels International has the support of the Department of Energy which says this project, when implemented, will enable Fiji to stand alone in the region in confronting the issue of increasing fuel costs. This will be the fourth project eyed to be established in Fiji to generate its own fuel two ethanol (cassava and sugarcane), two biodiesel (coconut oil and Pongamia oil). A brief prepared by Bio-Fuels International stated Fiji would be one of the major contenders among proposed sites in the South Pacific for Biofuel International's Renewable Energy Transformation Initiative. The brief stated that phase 1 of the development would see a cash infusion of more than $174 million to plant an estimated 100 thousand hectares of Pongamia in the first three years alone. According to the brief, the overall project is anticipated to tip the scales at $870 million over the next 12 years and cover a total plantation span of more than 500 thousand hectares of land.

Several other non-edible oil seeds are currently being explored by various entities for use in biodiesel. This includes another plant from India, neem, as well as the Chinese tallow tree. The neem seed contains around 30 percent oil, and India is one of the top neem oil producers. The Chinese tallow tree is a tropical perennial invasive weed in Florida, Texas, etc. The seed yield is 14 thousand kilograms per hectare, with an oil content of about 55 percent. The oil yield is about 7,700 kilograms per hectare (970 gallon per acre). Although they show promise, the neither of these are seeing the same type of attention as Pongamia, nor is Pongamia seeing the same type of attention as jatropha. In fact in June 2008, an article was published in the Jordan Journal of Mechanical and Industrial Engineering, comparing the methyl esters of jatropha, neem, and Pongamia. Pongamia was rated as the highest performer, followed by jatropha then neem.

Other non-food energy crops being investigated include crambe and cuphea, though are not receiving nearly the attention by media, governments or industry that is currently being seen by front runners such as jatropha and algae.

4.9 ALGAE

Algae are a growing area of interest for the production of hydrocarbons and lipids (algal oils) and recently added ethanol to this list. Oil-producing algae need to use stack CO_2 which offers one possible plus of algae production- algae as an off-gas CO_2 scrubber. Additionally, due to the high oil content in some species of algae, enough biodiesel can be made from 2 million hectares (4.95 million acres, 7,720 square miles, or 88 miles x 88 miles) to completely replace all diesel in the United States. Algae can be grown in seawater, minimizing the need for fresh water and land. Algae grow much quicker than terrestrial plants as well which is another plus.

There are several different options on how to cultivate and extract algae oil. Closed systems are being investigated by private industry and have been investigated by the DOE. Photo bioreactors (usually plastic bags) have been investigated as an option for cultivation as shown in Figure 4.28. This eliminates the possibility for contamination or an invasive species takeover. It is also mostly the surface of the pond that receives the light, so this also increases the surface area. This option has been tried and re-tried many times, and has not been found to be economic as of yet. In order to make this technology economic, co-products would have to be produced such as nutraceuticals.

Figure 4.28 Photo Bioreactor Algae Production system

Source: Vertigro

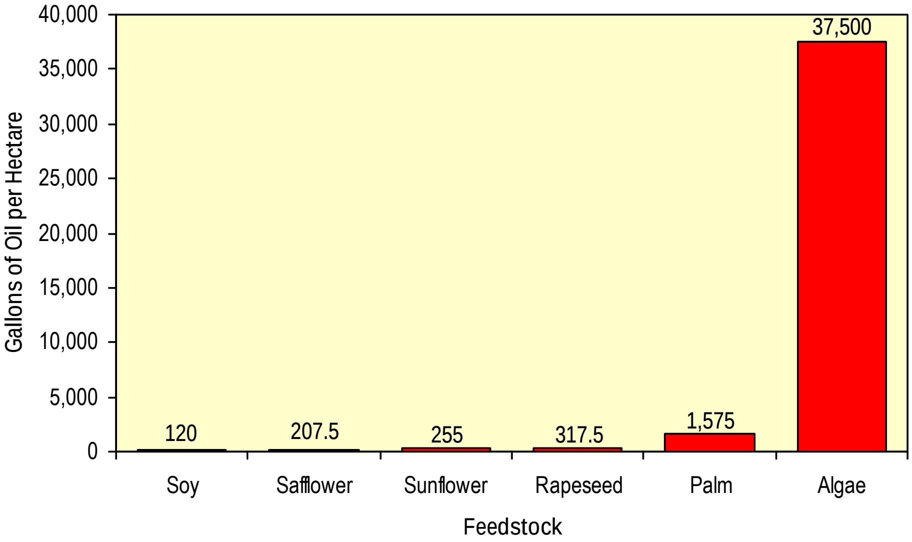
Another is the open pond. The open pond has the highest oil production per unit area – much higher yields than palm oil. It has the lowest biomass by-product. It is being widely pursued by multitudes of companies and governments, although none have yet been able to produce algal products economically except for the nutraceuticals industry. Figure 4.29 shows what open pond algae production looks like.

Figure 4.29 Open Pond Algae

Source: Seambiotic

For the most part, algae have been pursued for the oils contained within for the production of biodiesel, although in some cases, some companies have also sought to produce jet fuel from algae. This is due to the high oil content of some algae strains. Due to the production rate of algae, the high oil content, and way that it can be grown, algae has a very high potential oil production rate per hectare as shown in Figure 4.30.

Figure 4.30 Oil Production per Hectare of Oil Seeds and Algae



Algal oil separation is one of the challenges remaining for algae. In spite of the large potential for algae, no one yet has been able to bring a commercial scale algae biodiesel (or jet fuel) facility into existence, and make it economic.

One potential option to deal with this issue of algal oil separation, is to incorporate aquaculture into the process and to use an aquatic organism that feeds on algae (such as brine shrimp or tilapia) to transform the algae into a more usable and separable form. Although algal oil separation is not an established practice yet, fish oil separation is well known and well established. Aquatic organisms eat the algae, and the aquatic organisms are harvested and separated into products instead of the algae. Fish oil can be produced, as well as fishmeal. The fishmeal can be used as fertilizer or animal feed. The fish oil can then be processed into biodiesel.

The United States based company, Algenol, is trying developing a unique approach using algae. Instead of trying to get oil or hydrocarbons out of algae, it is trying to produce ethanol from algae. Algenol, with its “Direct to Ethanol” process, is attempting to produce 1 billion gallons per year from one facility, or almost 15 percent of current ethanol demand in the United States. To put this into perspective, a typical conventional world-class commercial ethanol plant is generally in the range of 100 million gallons per year. Algenol’s plant is to be located in the Mexican desert, using off gas from a local power plant. Initially it is slated to produce 100 million gallons per year which will be expanded to 1 billion gallons in subsequent years. Pemex, the Mexican state owned Oil Company has agreed to off take the ethanol produced. Production from this facility is scheduled for 2009, so until this facility in fact begins producing ethanol, it will not be publicly known if this is an economic process or if 1 billion gallons of ethanol from one facility is even possible or practical.

Due to the high production rate of algae coupled with the fact that algae can essentially act as a CO_2 scrubber if algae biofuels can be produced on a commercial scale, economically, it has the potential to be a game changer.

4.10 OIL YIELD

As already noted, biodiesel (FAME) can be produced from a wide range of fats and oils. The type and degree of pretreatment ahead of esterification is determined largely by the level of free fatty acids (FAA) the feedstock contains, but also by the presence of other contaminants, including suspended solids and odor compounds. In addition to plant-derived oils, animal-derived feedstocks can also be used, such as beef tallow and pork lard, which are byproducts of meat packing, fish oils and other fats generated by “waste rendering” of miscellaneous carcasses, such as from horses, diseased animals and road kill, which are outside the food chain. There tends to be a wider composition variation with animal sources than with plant oils. This is also true of waste oil, or yellow grease, which is primarily vegetable oil that has been used for cooking. Another characteristic of yellow grease is the relatively large amounts of FAA that have been liberated by heating in the cooking process. Trap grease (from factory and restaurant washings and drains), which is generally high in FAA and other contaminants, is a problem for industrial and industrial and municipal waste treatment. Ways of using such material to feed biodiesel production and in other ways are being studied.

Although most of the biodiesel projects in the United States and elsewhere are based on using virgin vegetable oils or waste fryer fats, other natural oil sources can and are being developed utilizing oils from plant sources that have not been attractive for cooking oil or oleochemical markets. United States Senate Bill S. 1058 that was introduced in 2001 includes in a definition of biodiesel oils from corn (maize), soybeans, sunflower seeds, canola, crambe, safflower, flaxseed and mustard seed, all common food and or oleochemical raw materials. However, many other plants have higher oil yields per unit growing area than these. More advanced feedstock sourcing concepts involve:

- Controlling and harvesting an invasive alien pest plant on the United States Gulf Coast (USGC), the Chinese tallow tree, which prolifically bears nuts with high yields of a high quality oil
- Raising, on poultry and swine manure and fallen animal caresses, the pre-pupae of the well-known and otherwise beneficial black soldier fly, which yield about 32 percent fat and 42 percent protein by body weight, are self harvesting, and can be processed in oilseed expellers
- Producing oil at high yields from particular species of algae in fresh water ponds

The global production (2006/07) of vegetable oils was: 35.76 million tons of soybean oil; 35.38 million tons of palm oil; 17.70 million tons of rapeseed oil; 11.21 million tons of sunflower seed oil; and 20.49 million tons of other oils. Soybeans are largely a Western Hemisphere crop. Palm is grown in Southeast Asia, particularly in Malaysia, but increasingly in Indonesia and South America. Rapeseed is grown primarily in Canada (where food varieties are known as “canola”, meaning “Canada oil”), and in Northern Europe. Sunflowers are primarily a European crop, while cotton is widely grown, but processed for seed oil primarily in the United States.

Nonetheless, many lesser-known oil-bearing plants that have higher oil yields are feasible. Some of the possibilities among the most commercialized ones are listed and compared to the common sources in Table 4.25. Of course, these are typical or average yields, and individual regions, economies, or farms may have very different yields. The typical yields per unit cropland of important oilseed corps are shown.

Table 4.25 Comparative Oilseed Yields

Plant	Seed Yield, lbs/acre	Biodiesel, gal/acre
Corn	7,800	18
Oats	3,000	23
Cotton	1,000	35
Soybean	2,000	48
Mustard	1,400	61
Camelina	1,500	62
Crambe	1,000	65
Safflower	1,500	83
Rice	6,600	88
Sunflower	1,200	102
Peanut	2,800	113
Rapeseed	2,000	127
Castor bean	-	151
Jojoba bean	-	170
Jatropha	-	202
Coconut[1]	3,600	287
Palm oil[1]	6,251	635
Algae, micro	-	1,850[2]

[1] yield in lbs of oil/acre

[2] based on actual biomass yields

As indicated, jojoba, a minor oil crop that grows in the desert, has a very high biodiesel yield. Similarly castor beans have high yields of oil, but this oil has toxic properties that are not a liability for fuel use but would be problematic for human contact. The Brazilian government has recently pushed castor bean biodiesel development to benefit rural economies, but has now withdrawn this initiative. The highest yielding plants, palm and coconut, are grown in the tropics.

On average, soybeans have a relatively low yield compared to some other feasible crops for biodiesel, but soybeans have the economic advantage (and complication) of yielding a valuable co-product from oil extraction, soy meal, which is an important components of feeds for poultry, swine and cattle as well as for other livestock and pets. It also has highly developed and efficient agronomy and product supply chains in the United States and Brazil. Besides whole soybeans serving as human and animal food, soybeans yield other foods and products such as edible oil, lecithin, soy protein, soy flour and soy hulls for fiber bran. In addition, being a nitrogen-fixing legume, it is used as a rotation crop for corn so that many corn growers are also soybean growers. Soybeans provide nearly 70 percent of the world’s protein meal consumption, with the next closest being rapeseed at 11 percent. None of the other oilseeds, except corn and perhaps peanuts have co-products with as much importance in human and animal nutrition and such other diverse economic uses.

4.11 FOOD VS. FUEL

Nexant estimates that using all fats, oils and greases reasonably expected to be available to produce biodiesel would replace less than 12 percent of the global diesel demand. Similarly for ethanol, converting all the current global starch resources would only replace half the gasoline, and also converting all the sugar resources would only contribute another five percent of the gasoline pool. One is forced to conclude, therefore, that to continue to make biofuels from grain starch, sugar and natural oils and fats resources, to their limits, even if the world were willing to completely deprive itself of these food substances, would not replace more than one-quarter of the expected petroleum fuel demand in 2015.

The amount of corn used for fuel ethanol in the United States has already grown so quickly as to equal and exceed exports. This is causing great concern among government agencies and non-government organizations that take an interest in world food supplies and pricing dynamics. However, only the starch component of grains is used in fermentation, and the byproduct of distillers dried grains and solubles (DDGS), which is minus this starch and consists mainly of protein, oil and fiber, is actually more nutritious for ruminants on a weight basis than grain. This is reflected in its typical price that is at parity or close to the price of corn or grain sorghum used to feed ethanol production. A similar situation prevails in the production of oil from oilseeds such as soybeans. For each bushel (60 pounds) of soybeans produced, only 10 pounds of extracted oil is used in making biodiesel. The other 50 pounds (the soy meal) is used to feed the hungry of the world as one of the best high protein foods available.

In addition, many of the world's hungry are also farmers. The poorest people will benefit more from the cultivation of biofuels if they are involved in the "value-added" stages of their production, such as processing and refining. In remote areas, poor farmers could benefit by producing their own fuels. As more economies become producers of biofuels, their rural economies will likely benefit as they harness a greater share of their domestic resources. Therefore, even though it is a growing concern for a potential clash, the "competition between fuel and food" is more complicated and perhaps less severe than many critics allow.

Logistics issues must also be considered. It is often said that there is enough food to feed the world's population, but that the problems are in ownership and distribution. Corn, cereal grains, dried casaba, oilseeds, and extracted natural oils generally can be stored and shipped distances, and are even traded between continents. Sugarcane, sugar beets, and biomass feedstocks are more bulky and perishable, so biofuels production facilities based on the latter need to be built near growing/harvesting areas. Some biofuels processing co-products, such as seed meals from oils extraction and DDGS from grain fermentation, can be stored and shipped to agricultural end users, while others, such as sugarcane bagasse or sugar beet pulp fiber must be used nearby the biofuels facility.

Increasing production of ethanol and biodiesel for fuel has already disrupted markets for cereal grains, oilseeds, and sugar. Food companies, commodity traders, and investors must attempt to envision how the biofuels industry will evolve in the coming years and what impact this will have on their own business so that they may plan for the future and cooperate in stabilizing these markets.

However, in the near term, developing ethanol and biodiesel fuels using conventional technology based on cereals, oilseeds and sugar can be viewed as the first generation of biofuels and is necessary to develop the demand and infrastructure for second-generation biofuels to come onstream. Ultimately this first generation will need to be supplemented by a second generation of biofuels obtained from "lignocellulosic" biomass, by fermentation, thermochemical processing or other advanced technologies. However, much of the latter technology is still in the laboratory or pilot plant stage of demonstration.

4.12 SUMMARY OF BIOREFINERY FEEDSTOCKS

As stated above, novel and innovative feedstocks for biofuels production are finding more attention in recent times, and are the subject of substantial investment and research. These investments and research are in turn being driven by the global demand for novel feedstocks with the most desirable qualities.

Key findings in regards to feedstock for biofuels production include:

- Though corn and sugarcane are still the predominant feedstocks for ethanol production as soy and palm oils are for the biodiesel industry, in the coming decades, this may not be the case. These food feedstocks may be replaced in the future with non-food competing feedstocks
- Non-food competing feedstocks are being sought and developed throughout the world and are in high demand as some economies will only approve biofuels projects that do not compete with food
- Many novel feedstocks for biofuel production are being investigated and used as alternatives to the traditional corn and sugarcane for ethanol and soy and palm oils for biodiesel
    - Key novel feedstocks being pursued for ethanol production include cassava, sorghum, waste cellulosics, and energy crops grown for cellulosic biomass such as misanthicus and switchgrass
    - Key novel feedstocks being pursued for biodiesel production include jatropha, algae, and waste oils.
- Jatropha is being widely pursued around the world and is receiving much attention. This has lead it to be poised to become a major feedstock to the global biodiesel industry
- Due to the sheer amount of resources available, research into waste cellulosics conversion may also create a paradigm shift when these technologies become commercially available
- Advances in feedstock development are being driven by sustainability, the food vs. fuel debate, land use, and climate change.
- Though not commercially viable yet, it is expected that should some of these feedstocks become commercially viable they will revolutionize the global biofuels market, and the global biofuels industry as a whole
- Advances in yield, disease resistance, and growth requirements are being researched in order to decrease farming costs and increase revenues

Section 5 Co-Products

5.1 INTRODUCTION

Co-products of biofuel production are an important part of biofuel production. The co-products can be sold to a variety of markets and in some cases have rendered traditional methods of production not as cost effective. Co-products often serve a vital role in the economic success of biofuels but they do not come without challenges of their own.

Disposal of some co-products is a valid concern as increased biofuels production have oversupplied the markets of some these co-products. Without a market for these co-products it can actually prove to be more costly to produce biofuels.

The following section discusses major co-products of biofuel processes, their uses, and any potential challenges in their disposal.

5.2 GLYCERIN

Glycerin is a major byproduct of biodiesel production by transesterification of vegetable oils or animal fats. About 10 percent by weight of biodiesel production is byproduct glycerin, resulting from the separation of the three-hydroxy group polyol backbone from the three fatty acid chains comprising the triglyceride feedstocks. Several of the technologies for FAME that have been discussed in this report produce glycerin byproducts.

As global biodiesel production expands rapidly, the industry is throwing off ever larger volumes of byproduct glycerin, to the extent that the glycerin market in Europe around 2003 became dominated by this byproduct glut as it overwhelmed byproduct production from other sources, such as oleochemicals and soap manufacturing from natural oils and fats. The price of refined glycerin fell by half from about \$0.70 per pound to just above \$0.30 per pound, and even lower at times. Crude glycerin prices have fallen to less than \$0.10 per pound, and essentially all of the world’s production of synthetic glycerin has ceased. At the same time, rising petroleum prices have led to a competitive advantage for natural oils and fats as feedstocks for soaps and detergents in competition with petrochemical alternatives such as linear alkyl benzenes (LAB), leading to even greater production of glycerin. Glycerin from oleochemical and soap manufacturing is generally of a higher quality than from biodiesel for various process reasons. Much early biodiesel capacity was built without glycerin refining.

This became an economic problem for early entrants into biodiesel production, as their investment return depended substantially on the byproduct credit from glycerin sales. Most investors are now counting on a much lower byproduct income as the collapsing market dynamic has become obvious. Clearly, the industry is eager to find new outlets for this glut of crude glycerin supply.

Existing and potential applications of glycerin (synonymous with glycerol and glycerin) as a physical ingredient, a molecular component, or feedstock for conversion, can be characterized in four categories based on physical and chemical properties and function:

- Physical Properties (humectant, sweetener, viscosity additive, low-glycemic food)
  - Existing – toothpaste, cosmetics, tobacco, diet/ snack foods, energy bars, etc.)
  - New and emerging – antifreeze, coolant, detergent, cattle feed supplement
- Chemical Feedstock
  - Fermentation – 1,3 propanediol (PDO), Polyhydroxyalkanoates (PHAs), etc.
  - Dehydration
  - Hydrogenolysis – PG manufacture
- Chemical Reactivity (monomer)
  - Fatty esters for food applications (e.g., glycerol monostearate additive)
  - Polyglycerols – drilling fluids, lubricants
  - Unsaturated polyester resins (UPRs)/Alkyds – cross-linker/monomer
  - Polyols – for polyurethane resins (PURs) (polyester monomer and polyether "starter")
- Fuels – Direct/other fuel cells, glycerol *tert*-butyl ether (GTBE) motor fuels additive, combustion (boilers, gas turbines, cement kilns, etc.)

Since crude glycerin is the actual byproduct of biodiesel manufacture, adding refining capacity for converting crude to refined grades such as USP, Kosher, other fine chemical grades, and industrial grades, is a challenge in a down-price market. Therefore, there is great interest in finding and /or developing applications for crude grades.

Most short-term growth potential is based on physical, not chemical properties. The chemically-determined "molecular" applications, such as in UPRs and polyester polyols for PURs, show little growth potential. Nonetheless, for the longer term, many chemical companies are examining the possible chemical derivatives ("molecular conversion" opportunities) for glycerin as alternatives to potentially permanently higher priced petrochemical feedstocks. Some of these potential routes are already commercialized, while others are only under development or examination.

Salient glycerin derivatives include:

Commercialized Derivatives Routes

- Polyglycerols – many applications in lubricants, oil and gas drilling, construction materials
- Oxidation of glycerol
  - Glycidol – stabilizer for natural oils and vinyl polymers
  - Glyceric acid

Developmental Routes/Products

- 1,3-PDO
- Epichlorohydrin

- Propylene glycol (refer to PERP 06/07-S4, *Glycerin Conversion to Propylene Glycol*)
- GTBE – diesel/biodiesel additive and/or gasoline oxygenate additive
- Esterification of glycerol
  - Glycerol carbonate – potential precursor for glycidol
  - Various glycerides – some monoglycerides of fatty acids have been registered as mild biocides, acaricides
- Hydrogenolysis of glycerol is also feasible (Shell Patent US 6,080,898) - leads to mixtures of acrolein, *n*-propanol, 1,3-PDO and PG (note that acrolein is an intermediate for the important chemicals, acrylic acid, methionine, and 1,3- PDO)
- Dehydration of glycerol to acrolein
- Fermentation products may include:
  - PHAs (natural polyester – covered by a Metabolix, Inc. patent)
  - Succinic acid
  - Itaconic acid

In addition to these molecular conversion opportunities, glycerol presents a number of opportunities for substitution for propylene glycol and sorbitol without conversion (generally as USP or industrial grades), as well as other emerging or proposed high volume opportunities in crude, refined, or semi-refined forms.

Near-term opportunities to substitute glycerin for PG and sorbitol are few but large, despite the strong price drivers. Rather than by price, many potential expansions of existing glycerin applications are driven more by properties, precluding or limiting expanded use. There are also often other types of practical impediments to substitution, including process issues (such as viscosity limitations), regulations, equipment changes needed, lack of experience, customer uncertainty as to permanence of price differences, etc.

The main areas of switchability are in liquid detergents, toothpaste, and coolants/antifreeze (heat transfer and freezing point suppression), and personal care product makers could feasibly use more glycerin where it was not formerly used, such as in soaps, etc. Nonetheless, “competition” from glycerin is still limited among PG makers, because of robustly growing PG demand, especially in Asia (driving exports from the West), and the high level of capacity utilization in PG plants. In addition, since the market for PG’s precursor, propylene oxide, is primarily determined by the robust market for its predominant derivative, polyurethane foams and other polymers, manufactures of PG are unlikely to mount a price-lowering competitive response. In a “macro” view, “the world will be short by tens of thousands of tons per year of “glycols” (PG, polyglycols, polyglycerols, etc.), and glycerin could help “close the gap”, according to industry experts.

5.3 DRIED DISTILLTER GRAINS WITH SOLUBLES (DDGS)

Dried distiller grains with solubles (DDGS) is the dried residue remaining after the starch portion of the grain is fermented in the ethanol production process. The drymill ethanol production process utilizes only the starch portion of the corn, which is about 70 percent of the kernel. After complete fermentation, the alcohol is removed by distillation and the remaining fermentation residues are dried. The remaining grain nutrients are protein, fat, minerals, and vitamins which are concentrated into the DDGS.

DDGS is most often sold to famers as it is a rich source of vitamins and is lowest in fiber and highest in fat making it an excellent food source for multi-stomach ruminates. However, livestock such as swine and poultry, have very different digestive systems and do not tolerate DDGS as well as their multi-stomach ruminate counterparts.

Because most corn dry mill ethanol plants are far from the DDGS byproduct market of cattle feed and animal feed preparation, the distillers' grains residue must be dried for storage and transport, otherwise the material would quickly spoil and become unusable. Ideally, the more economically attractive option is to integrate the ethanol production with adjacent or nearby livestock feeding operations, so that wet material can be produced and the capital and operating cost (primarily heat energy for drying) can be saved. Realistically, given the amount of forecasted DDGS product, most distillers' grains residues will be dried for more economic and efficient transport.

With the increased production of ethanol over the past few years DDGS production has increased significantly. On the small scale DDGS is considered a positive energy and monetary benefit as it can be sourced as animal feed and a power feedstock. However, as ethanol production has increased dramatically over the past few years caused by shift to alternative fuels, DDGS production has also raised significantly. On the large scale DDGS can be a serious waste disposable problem. While production of these byproducts can produce some positive net energy benefits the energy needed to dispose of the excess would greatly outweigh the benefits.

In the US increasing exports of DDGS is vital to the continued success of the US ethanol industry. Sales of DDGS have become critical in maintaining ethanol plant profitability as ethanol margins have become pinched in recent times. The US Grains Council has been working to raise global awareness of the use of DDGS in animal feed with hopes of generating more demand and increase exports.

5.4 SYNGAS

Syngas is an important intermediate produced by biomass gasification. It consists mainly of hydrogen and carbon monoxide with small amounts of carbon dioxide and water. Reaction conditions of the thermochemical process can modify the final composition of syngas. Syngas can be used to produce synthetic natural gas, liquid biofuels, renewable chemicals, hydrogen, or can be burned to produce heat and energy to support a process facility or for sale to third parties or the grid.

The syngas can be converted by Fischer-Tropsch (F-T) synthesis to diesel-range fuel fractions, waxes, LPG, and naphtha for cracking to olefins for chemicals or polymers synthesis. Hydrogen can be removed for hydrocracking purposes by converting the syngas via the catalytic water-gas shift reaction to hydrogen and carbon dioxide.

While the commercial production of chemicals from syngas typically uses metal catalysts, there has been some work done biosyngas fermentation. Several genera of microorganisms are capable of consuming syngas rather than the typical sugar substrates as part of their metabolism to produce chemicals such as ethanol and other products (e.g. acetic acid.)

5.5 CARBON DIOXIDE

Carbon dioxide (CO_2) is a co-product of drymill ethanol production. It is produced during the fermentation stage of ethanol production and is sometimes collected and marketed as a co-product. If the CO_2 is sold it is cleaned of any contaminants, mainly residual alcohol, and compressed to its liquid state for shipping. In cases where there is no market for the CO_2, it is processed and vented to the atmosphere.

CO_2 is also used for beverage carbonation, refrigeration of food products (dry ice), and food preservation (flash frozen meat). It can also be used as a shielding gas for welding and can be injected into difficult or aging oilfields for enhanced oil recovery.

Some believe that the carbon footprint of ethanol production is too big with all the excess CO_2 that is produced. Scientists have claimed that the crops planted as feedstock for ethanol produce would negate the CO_2 produced by absorbing the CO_2 while growing. Those who are skeptic believe that the dedicated corn to ethanol crops do not negate the CO_2 produced during the process since unaccounted for carbon footprints left during the planting and harvesting of the crops is not negated.

5.6 CARBON SEQUESTRATION AND BIOCHAR

A strategy known as “Terra Preta”, or agriculture practiced with biomass carbonization with carbon burial, is growing in scientific, technical, and policy-making interest. Biomass may be pyrolyzed by heating in low oxygen atmospheres to achieve a partition to activated biochar and “Bio-oil”, a highly active and unstable oxygenated hydrocarbon by product that can be gasified or more directly upgraded to biofuel. The process of pyrolysis is also called “torrefaction”, which is the French word for roasting various organic materials such as coffee or, in this case, woody biomass. The biochar burial serves to take carbon out of the atmosphere, or, as the Amazonian Native Americans found centuries before, also serves to hold nutrients and water in the soil, and to enable greater agricultural productivity.

Scientists have concluded that for thousands of years parts of the Amazon have been managed to sustain productive agriculture and at times, sustain dense human populations. It is estimated that more land was under cultivation in the Amazon on the eve of the arrival of Columbus than is today. The fact that certain forms of agriculture are possible is a vital consideration for the sustainable, economic development of tropical rainforests.

In Brazil, by government estimates, some 50 million hectares of degraded but arable pasture could be used for soy and cane cultivation. More rational utilization of already cleared and degraded areas, combined with intensification of soy and cattle production, can help reduce the need to clear forest land, and thus reduce the risk that biofuels production might not be sustainable in Brazil and similar regions.

Biochar sequestration can be considered not merely carbon neutral, but actually a *carbon negative* strategy, because it results in a net decrease in atmospheric CO_2 and other GHGs over long periods. That is, rather than allowing biomass (which removes carbon from the atmosphere to grow) to decompose and re-emit the CO_2 or even produce more potent methane under anaerobic conditions, or by being eaten by termites, etc., pyrolysis will sequester the carbon. This will remove circulating CO_2 from the atmosphere and store it in virtually permanent soil carbon pools. In addition, the bio-oil produced can be used to displace fossil liquid fuels, further reducing the net emissions of CO_2. Pyrolysis also provides an opportunity for the processing of agricultural residues, wood wastes, and municipal solid waste into useful clean energy. Although some organic matter is necessary for agricultural soil to maintain its productivity, much of the agricultural waste can be turned directly into biochar, bio-oil, and syngas. The pyrolysis transforms such organic material into three main components: syngas, bio-oil, and the biochar (which contain about 60 percent of the carbon contained in the biomass).

In addition to its potential for carbon sequestration, biochar has several other advantages:

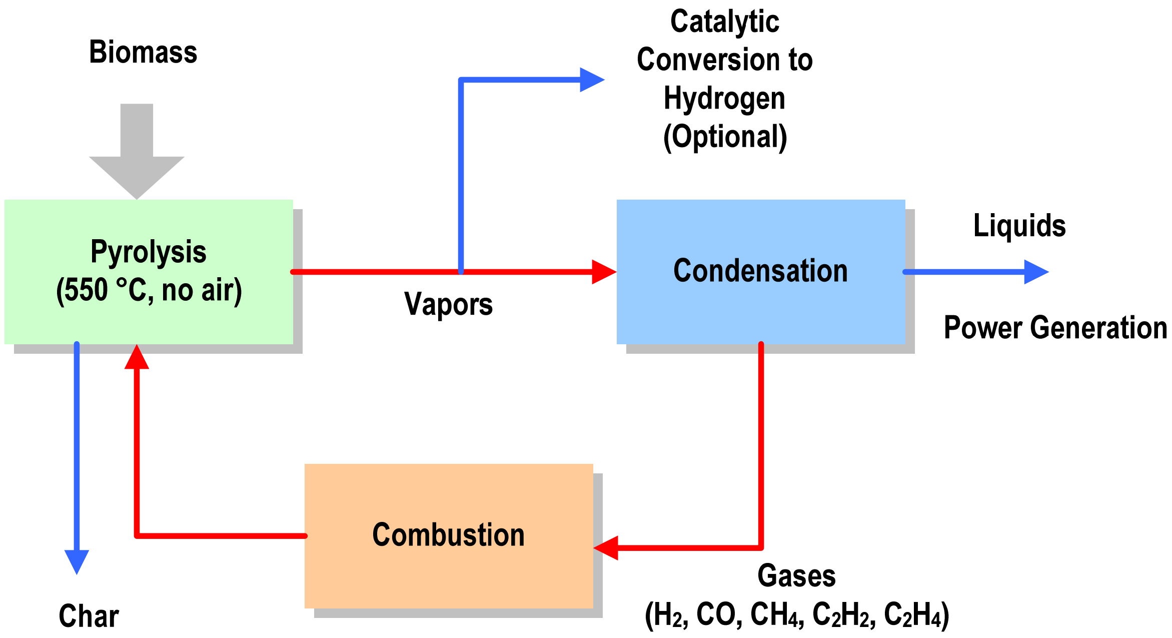
- Can increase the available nutrients for plant growth, water retention and reduce the amount of fertilizer by preventing the leaching of nutrients out of the soil
- Reduces methane and nitrous oxide emissions from soil, thus further reducing GHG emissions
- Can be utilized in many applications as a replacement for other biomass energy systems
- Can be used as a soil amendment to increase plant growth yield

Figure 5.1 is a schematic of the process for biochar production. Biochar can be produced by either fast pyrolysis or slow pyrolysis. The biochar yield is higher, typically more than 50 percent, in slow pyrolysis the processing can require hours to complete. Fast pyrolysis, in contrast, has a 20 percent biochar yield, but needs only seconds of residence time for complete pyrolysis. Fast pyrolysis typically has a 60 percent yield of bio-oil and 20 percent of syngas.

The essential features of a fast pyrolysis process are:

- Very high rate heating and heat transfer, so typically requires a finely ground biomass feed
- Carefully controlled reaction temperature, about 500°C in the vapor phase, and vapor residence time of less than 1 second
- Quenching (rapid cooling) of the pyrolysis vapors to condense the bio-oil product

Figure 5.1 Production of Biochar



Q109_01357.001.01-S7.vsd

Source: Biochar and its Role in Mitigating Climate Change, S. Zafar, Dec.17, 2008

Bio-oil is a dark brown liquid with compositions reflecting the biomass feedstock. It comprises a complex mixture of highly active and unstable oxygenated hydrocarbons. It has a much higher physical density than woody materials (three to six times, depending on the type) and a higher energy density, which reduces logistics costs. It is not suitable for direct use in standard internal combustion engines, but must be upgraded by various means to stabilize and deoxygenate it and reduce its acidity. It can, however, be burned with less upgrading in a stationary combustor, especially in co-firing applications because it can be more readily handled and burned than solid biomass and is cheaper to transport and store. These options have been found technically feasible. In addition, bio-oil can yield a wide range of organic compounds and specialty chemicals.

Alternatively, the bio-oil can be upgraded to either a diesel range engine fuel or through gasification processes to a syngas and then biodiesel or biogasoline products.

5.7 SUMMARY OF BIOFUEL CO-PRODUCTS

As stated above, biofuel co-products are an integral part of biofuels production.

Key findings in regards to co-products of biofuels production include:

- Biofuel co-products can be sold for a variety of end uses including:
  - Glycerin as a substitute ingredient for personal care products

  - DDGS as cattle feed
  - Syngas as a feedstock for chemical production
  - Carbon dioxide as a method of food preservation
  - Biochar as a fertilizer to enrich carbon content in soil
- Despite their many end uses, biofuel co-products run the risk of being oversupplied to their markets with increased biofuel production
- Without an end market to sell to, co-products can become more energy intensive and expensive to dispose of
- Concerns of this co-product supply/demand balance are realized and efforts are being made to ensure market demand for these co-products

The world energy supply is facing a diverse and broad set of challenges. Demand for petroleum continues to increase, but the rate of new crude oil discoveries is declining. Concerns over climate change related to carbon emissions are affecting APEC member economies' policies and strategies. Combined with other drivers, these factors are putting increased focus on bio-refinery processes and sustainable hydrocarbon fuels made from biomass.

Based on the above concerns, an APEC Workshop on Implications of Bio-refineries for Energy and Trade in the APEC Region was held on 7-9 October, 2009 in Chinese Taipei. More than 90 biofuels scientists and engineers from 12 APEC member economies, representing academia, industry, and government agencies, gathered in Chinese Taipei to discuss bio-refinery technologies for making hydrocarbon biofuels a practical reality in the future. The substantial interest in this workshop, evidenced by the diversity of participants, demonstrates the vital importance of this topic to APEC member economies.

The objective of the workshop was to articulate the suggested biofuels trade and the critical role that chemistry, chemical catalysts, thermal processing, and engineering play in the conversion of lingo-cellulosic biomass into biofuels, including "green" boiler fuel, gasoline, diesel, and jet fuel made from bio-refinery processes. For readers who are interested in the presentation materials of the workshop, the workshop agenda is attached in Appendix B and the presentation slides can be found at the website http://www.netd.itri.org.tw/apec_biorefinery2009/Presentation.html.

Several issues and comments concerning the bio-refinery technologies over the presentations and discussions in the workshop had been raised up. The main issues and comments on bio-refinery technologies are summarized as follows:

- Availability of non-food feedstocks and cost-effective cultivation system should be studied for bio-refinery technologies.
- Cost-effective bio-refinery processes and products should be studied and evaluated; however, the technologies used should consume energy efficiently and generates no additional environmental impact.
- Need strong government incentives and supports for biofuels production and trade in the APEC region.
- Distribution, retailing and vehicle compatibility of biofuels should be evaluated.

A roundtable discussion followed up the workshop presentations was then set up to gather the comments and suggestions from experts and audience. To assist the roundtable discussion, five major topics reflecting the above issues and others have been chosen by chair and co-chairs of the workshop for the roundtable discussion, including:

- What are your suggestions for the promotion of bio-refining and related trade?
- What is needed to link bio-refinery emission reduction with carbon credit?

- In what way can distributed bio-refineries help develop zero emission communities?
- What is needed to promote the trade of feedstocks, intermediates and final products from bio-refineries?
- Provide your top 2-3 needs for the promotion of trade and bio-refinery technologies for use in defining follow-up actions.

The following summarizes the comments and suggestions from this roundtable discussion.

6.1 WHAT ARE YOUR SUGGESTIONS FOR THE PROMOTION OF BIO-REFINING AND RELATED TRADE?

Participants called for government measures that would provide a more balanced fiscal environment for the promotion of bio-fuels and other sources of renewable energy versus traditional fossil fuels. Specific proposals that were put forward included:

- Carbon taxes should be introduced to discourage usage of fossil fuels and incentives provided for carbon capture and storage to encourage the development of green energy and the protection of rainforests.
- The removal of subsidies for fossil fuels, especially subsidies for coal mining and crude oil production.
- Government support and incentives throughout the complete product value chain for both bio-fuels and other renewable energies. These would address the needs of end-users as well as industry suppliers in meeting environmental improvement targets.

Participants were particularly focused on the issues of moving the 'first generation' biofuel technologies from editable crop feedstocks to the 'second generation' bio-refinery technologies from non-food feedstocks and the development of sufficient scale to achieve critical mass as an energy supplier. A variety of collaborative measures were proposed to achieve this goal and related trade in the APEC region.

- Collection and sharing of data between APEC member economies, especially on the development of non-food biomass production. This would encourage the development of 'second generation' biofuels by accelerating research and development on the selection and availability of feedstock and related process technology.
- Developing an inventory of feedstock availability and development, especially in non-food biomass including jatropha, algae, forest products, agricultural residues and waste products such as Municipal Solid waste (MSW). There was abundant feedstock but limited data on how much it costs to produce and collect.
- Cost-effective biomass collection systems need to be established to support large-scale bio-refineries.
- Encouragement of 'first movers' was needed to achieve take-off in 'second generation' bio-fuel production. It would be difficult to move to the bio-refinery technologies until the feasibility of related technologies had been proven. Participants suggested that APEC could provide assistance in establishing demonstration bio-refinery feasibility studies that would encourage early entry by prospective industry investors.

- Participants were also concerned with the definition of bio-refining and all the co-products it produces and the practical issues of integrating bio-refining with existing oil refineries in a way that enabled the refiner to calculate and obtain carbon credits as an incentive.
- There was also interest in promoting joint industry-government projects.

In the longer term, participants were conscious of the importance of developing bio-fuels and other bio-products as internationally traded commodities and the need to put in place the necessary tools to achieve this.

- The development of international trade in bio-refinery products, which was discussed in detail in Topic 4 below, would be needed to justify large-scale bio-refinery development.
- Identifying likely trade flows for feedstock and products both in APEC and worldwide was suggested as an initial planning study.
- Establishing guideline specifications for bio-fuels, for example, ‘green diesel’ and ‘green jet fuel’, and product compliance to internationally accepted and harmonized standards would be critical for international trade to develop. Standards for international trade would probably need to be more stringent than standards for domestic use.
- It would also be necessary to determine at what level accepted standards would apply and would they include components.
- As well as standards, the bio-refining industry needs to develop ‘best practices’ and a code of practice to accompany any trading system.
- Long-term commitment from industry, government and academia would be needed to create demand and sustain confidence in international trade opportunities.

Overall, participants recognized that the promotion of bio-refining and related trade required them to look at all aspects of a long and complex value chain.

Preparation of educational programs and promotional materials to promote the use of bio-fuels was also a recurrent theme among participants.

6.2 WHAT IS NEEDED TO LINK BIO-REFINERY EMISSION REDUCTION WITH CARBON CREDIT?

Establishing baselines against which a bio-refinery could demonstrate emission reductions eligible for carbon credit was a prerequisite for extending any carbon credit system to bio-refineries.

- Participants were particularly interested in the development of Life Cycle Analysis (LCA) as a means of determining emission reductions as a basis for obtaining carbon credits. This would also require standardization of LCA methodology.
- Participants believed it would be difficult to calculate baselines for carbon credit on the historical trends of CO2 emissions without the cooperation of the oil industry.
- Baselines were needed not only to calculate emission reduction but also to allocate the carbon credit to the various players in the supply chain.

- It was suggested that land use impact assessments in each economy were vital to the development of baselines and to track emission reductions in the total system.
- Participants also referred to the UN Framework Convention on Climate Change (UNFCCC), the Kyoto Protocol and the issue of Certified Emission Reductions (CERs) under the Clean Development Mechanism (CDM) by which developing economies can earn CERs that can be sold to industrialized economies. Participants were also aware of the work of the CDM Executive Board and the Joint Implementation Supervisory Committee in working out methodologies and baselines for establishing emission reductions.
    - It was noted that in the Philippines, the law on bio-fuels provides tax exemptions for income from carbon credits and that the Department of Energy recommends projects that reduce emissions to get tax credits.
    - It was also noted that economies needed to identify who has benefit from CERs in the product flow from planting to producing to using.

Once the baselines for emission reduction by bio-refineries had been established, there needed to be a system for commercializing carbon credits.

- An Emission Trading System would have to be established, including documentation/certification of the source of feedstock, the converting process, the blending process and a procedure of random product testing to police the system.
- Participants acknowledged the need to work with carbon markets and with governments to gain recognition from existing Environmental Credit Markets, for example, the Renewable Energy Credit Markets (RECs), the Carbon Off-set Markets (COMs) and Emission Allowance Markets (EAMs).

6.3 IN WHAT WAY CAN DISTRIBUTED BIO-REFINERIES HELP DEVELOP ZERO EMISSION COMMUNITIES?

Participants were interested in two models of ‘distributed bio-refineries’. The first model is the ‘Biomass Town’ concept that has been developed in Japan and by July, 2009 already involves 217 communities out of a targeted 300. The Biomass Town concept is based on the development of small bio-refineries as part of a community project to achieve zero emissions.

- Participants were particularly interested to learn how carbon credits could be applied on a community scale rather than a single plant.
- Participants recognized that development of the Biomass Town concept would empower involvement of local governments to support emission reduction goals and suggested the mechanism to be adopted should be supported by Life Cycle Analysis.
- Participants were interested more broadly in the concept of local production and local use as a lever for developing local biomass resource. This could include waste-to-energy programs and the reduction of unutilized energy.

- Overall the development of ‘Biomass Towns’ needed education and promotional programs to disseminate information and encourage community action. It also required a good inventory of biomass resources.
- It was also suggested that the goal should go beyond zero emission by promoting the introduction of carbon capture and storage (CCS) technology, including both cellulosic CCS and algae CCS.

The second model of ‘distributed bio-refineries’ relates primarily to multi-level feedstock collection systems to support a large-scale bio-refinery, be it a self-standing facility or an expansion of an existing oil refinery.

- In many APEC economies, the cost-effective collection of bio-refinery feedstocks is a major economic barrier, especially in the case of low energy density feedstock that requires collection over a wide area and may impose heavy transportation costs on local feedstock growers. Thus, a multi-level collection system at local, provincial and regional level is needed to build capacity and establish infrastructure.
- Participants were interested in the development of pyrolysis platforms as a means of integrating widespread biomass feedstock collection with the existing production infrastructure of oil refineries on a cost-effective commercial scale.
- Engagement with local communities is again needed to achieve a balance between supply and demand and to share information on energy, environment and economic benefits from bio-refineries.

6.4 WHAT IS NEEDED TO PROMOTE THE TRADE OF FEEDSTOCKS, INTERMEDIATES AND FINAL PRODUCTS FROM BIO-REFINERIES?

Advance planning was needed to promote and facilitate the development of trade related to bio-refineries.

- Participants discussed the need to identify potential products and product flows both within APEC and with non-APEC economies and also identify and address potential barriers to trade, both behind the border and cross-border.
- International trade development would need standardization and harmonization of product specifications among APEC economies.
- In addition to accepted standards, APEC economies would need to align their policies to allow opportunities for trade.

Participants recognized that trade related to bio-refineries encompassed not only bio-fuels but also feedstocks and multiple co-products of high value, such as chemicals, and thus they had to develop linkages across a diverse range of potential markets.

- Transparency and good communication was needed to match up trade opportunities in these multiple product sectors.
- The potential market for some co-products is probably limited and assistance may be needed to link co-products to markets.

- It would be useful to have information on each APEC economy's experience on feedstock, fuel products and bio-refinery technology.
- It was suggested that the APEC website could be used to advertise trading opportunities.

Participants believed that development of international trade would require participation from both governments and multi-national global companies

- Bio-fuels for transportation would only achieve a large enough scale for international trading if they were supported by the major oil refiners and the major auto makers

Participants also identified some specific issues facing trade development.

- To trade feedstock such as raw biomass (e.g. rice straw, rice husk and bagasse), it was necessary to reduce the density of the raw biomass for bio-refineries.
- For inland trade, there needed to be the development of equipment and facilities adapted for small trucks that could operate in mountainous regions.
- Auto-makers would have to check specifications and gain approvals before using bio-fuels.

6.5 PROVIDE YOUR TOP 2-3 NEEDS FOR THE PROMOTION OF TRADE AND BIO-REFINERY TECHNOLOGIES FOR USE IN DEFINING FOLLOW-UP ACTIONS?

Participants had many diverse views on the top needs for promotion of trade and bio-refinery technologies. These partly reflect the diversity of background and needs of individual APEC economies and partly the many drivers that are at play in the bio-refinery product value chain. Participants were therefore more concerned with establishing the processes for pushing forward on a broad front rather than a narrow focus on two or three items.

- Participants thought APEC was a good forum for exchanging knowledge and technologies and for providing guidance on policy making as well as influencing investors and the general public. Collaboration through APEC would help to accelerate the promotion of bio-refinery technologies and related trade.
- Specific information-gathering proposals for consideration as APEC projects included:
    - A study of potential trade in bio-refined products that would identify materials and likely product flows within and beyond APEC, including possible barriers and solutions.
    - Compiling an inventory of biomass feedstock and information on existing bio-refinery technology options.
    - Identifying suitable locations for 'distributed' bio-refineries in terms of configuration, scale and local integration.
- Participants also called for a continuation of APEC workshops on bio-refining and related trade, which would encompass all the various stakeholders in the development of the industry, including forums for

  - Policy makers concerned with fiscal support, regulations, product standards and harmonization and trade policies
  - Technology issues especially concerned with capacity building for second generation biomass feedstocks
  - Trade development issues

Participants were aware that development of bio-refineries and related trade required government involvement, especially in the development of 'second generation' bio-fuels and co-products. Specific targets for government participation included:

- Improvements in the fiscal environment which would include carbon taxes to discourage fossil fuels and incentive payments to reward carbon capture and storage technologies, including forest conservation and reforestation.
- Government assistance in establishing the 'early day' demonstration of a commercial scale plant using 'second generation' feedstock.
- In the debate for government funds, to put the case to prioritize biomass as a feedstock for bio-fuels ahead of power generation.
- At the same time, while some participants welcomed the power of governments to drive development and even regulate prices, other participants were concerned that the development of the industry should not become over-dependent on government intervention that could also be reversed.

Some participants focused on the development of international trade as being the ultimate driver of commercial scale bio-refineries.

- International trade development depended on the establishment of standards. Since APEC is very much concerned with trade development, it was suggested that APEC's Trade and Liberalization Fund (TILF) could be used to fund a project for preparing bio-fuel product standards.

Other participants focused on issues of scalable developments and private sector involvement

- Cost-effective biomass collection systems were needed both for local scale bio-refineries and for larger scale bio-refineries within existing oil refineries.
- To the extent that large scale 'second generation' bio-refining depended on integration technologies with existing oil refineries, there need to be both research and development on technological issues and also on fiscal issues of attributing emission reductions and carbon credits
- Commercial scale development of bio-fuels could probably not be achieved without private sector co-operation from oil refiners and auto-makers.

7.1 CONCLUSIONS

Bio-refinery technologies and their status have been discussed in the report above. Nexant and Industrial Technology Research Institute (ITRI) have made the following conclusions based on the study and the presentations given at the APEC Workshop on Implications of Bio-refineries for Energy and Trade in the APEC Region on 7 – 9 October 2009 at Taipei.

- With the growth in the current mode of ethanol production by fermentation of grain and sugar feedstocks, comprised of corn, wheat, other major coarse cereals, sugarcane and sugar beets, dislocations are likely to occur in world food and feed markets; to avoid these, similar starch and sugar crops such as sorghum and cassava will be further developed in agriculture and processing technology
- An attractive optional solution for extending ethanol production is in using emerging technology to convert biomass wastes such as corn stover, wheat or rice straw, or sugarcane biomass (field waste and bagasse) to fermentable sugars
- The next level of options include making ethanol by fermenting sugars derived from switchgrass or higher-yield “energy cane”, implementation of which will require development of a new agriculture, including extensive new switchgrass origination systems and supply chains, and modification of the current sugarcane agricultural model; much general and specific attention is being paid to these options (e.g., in the US and Brazil)
- In the longer term, as ethanol becomes a more significant petroleum replacement, to relieve logistic constraints (whether ethanol is made from grain, sugar or biomass), industry will most likely convert it to hydrocarbon gasoline fractions in integrated facilities, or make higher alcohols such as butanol instead
- Additional longer-term options include biomass gasification to make syngas for catalytic syntheses to produce gasoline fractions or higher alcohols (so-called “biomass-to-liquids” or BTL)
- Biobutanol is already a commercial technology (ABE – *clostridium*-based fermentative co-production of acetone, butanol, and ethanol) that only needs to be re-instated and improved
- Biobutanol is most likely to be more widely commercialized by taking market share from synthetic butanol in the industrial chemical and solvent markets before it achieves market share as a fuel at lower prices
- Hydrocarbons are the components of gasoline, diesel, and jet fuel; by using synthetic biology to either alter existing microbes or build new ones, these new microbes in fermentations can be made to produce hydrocarbons that directly or through further processing yield fuels that are more compatible with the current infrastructure than alcohols or ester-based biodiesel

- Gasification can be used to convert the by-products and residues from other biofuel processes as well as from the agricultural value chain that supplies these processes and agricultural, forest products, and food processing biomass wastes in general
- The current version of biodiesel, fatty acid methyl ester (FAME), is most likely a "transition" technology, which, though it can make an attractive venture given tax incentives currently in place, ultimately cannot substitute significantly for petroleum diesel in the marketplace because of feedstock limitations orders of magnitude more severe than for ethanol
- Biodiesel made by emerging technologies to hydrocrack triglycerides (fats and oils) in refineries (i.e., NExBTL and H-Bio), has improved potential for economy of scale, more rapid development, makes biodiesel more attractive for refiners' involvement, and integrates better with the refining and vehicle infrastructure, and will likely be adopted widely in the near term
- In the longer term, synthetic diesel from biomass (made via gasification followed by F-T conversion) is likely to be more economic than conventional biodiesel, with low feedstock costs, substantial by-product credits, and great economies of scale - but the product is also essentially as toxic and non-biodegradable as fossil resource-derived diesel fuel
- FCC technology can be used to convert biomass and other biofuels materials to hydrocarbons that are more compatible with petroleum and petrochemical operations and with conventional vehicle fueling systems
- Other technologies that use different methods of producing biofuels include technologies from Virent (Aqueous Phase Reforming), Terrabon (lime pre-treatment, organic acid hydrogenation) and Zeachem (acetic acid fermentation with hydrogenation)
- Bio-refineries will incorporate biomass conversion equipment and processes to produce fuels, power and chemicals from a biomass feedstock, utilizing the value of different components in the biomass feedstocks and intermediates

- The two largest consumers of water during the corn ethanol life cycle are water consumption in crop feedstock production and the corn ethanol production process

- Energy and water demands of ethanol processes are closely integrated and one way to reduce water demand is to reduce energy consumption

- Steps to reduce water requirements in ethanol production are being researched as water usage and supply are becoming growing issues in many economies. Methods include utilizing alternative heat transfer mediums, such as forced-air fans for cooling instead of cooling water

- Cellulosic ethanol from biochemical processes requires the most water with a ratio of 6:1 water to ethanol. Dry mill ethanol requires a ration of water to ethanol of somewhere between 3:1 and 4:1 and cellulosic ethanol via thermochemical routes water to ethanol ratio averages out at around 1.9:1.

Other conclusions in respect to APEC member economies include:

- Fermentation of sugar, starch and grain continues to dominate in the US as most commercial scale plants in the area employ this type of technology
- Commercial lignocellulosic ethanol soon may become a reality as several commercial scale lignocellulosic feedstock based bio-refineries are being built in the US
    - Abengoa Bioenergy Biomass, LLC (Hugoton, Kansas) – converting lignocellulosic feedstocks (corn stover, wheat straw, sorghum, switchgrass) to produce both ethanol and syngas, with 11.4 million gallons of ethanol per year. Also co-producing steam for cellulosic ethanol operations and excess steam for corn ethanol plant nearby. Estimated construction and start up in 2010 and 2012, respectively
    - Range Fuels (formerly Kergy Inc.) (Soperton, Georgia) – converting biomass (comprised of unmerchantable timber and forest residues) to produce 935 thousand gallons of ethanol and 935 thousand gallons of methanol. Using pyrolysis followed by thermal reforming of pyrolysis vapors for biomass conversion. Estimated start up is the first quarter of 2010
    - Poet (formerly Broin Companies) (Emmetsburg, Wisconsin) – converting lignocellulosic feedstocks (corn cobs and/or corn fiber) to produce 25 million gallons of ethanol per year. Integrating the production of cellulosic ethanol into a dry corn mill process. Production is estimated to start in 2011
    - BlueFire Ethanol, Inc. (Mecca, California) – converting biomass (comprised of sorted green waste and woody waste from landfills) to produce 19 million gallons of ethanol per year. Using their concentrated acid hydrolysis technology followed by fermentation for biomass conversion. Facility will be located next to a 47MW biomass fed power plant. Project is currently delayed
- Other organizations are reported to be researching lignocellulosic-based ethanol production via fermentation routes or planning projects based on various types of biomass, including Iogen (Canada/United States), Dedini (DHR Process, Brazil), Abengoa Bioenergy (Spain), and BCI (United States)
    - Iogen is successfully operating a facility in Ottawa, Canada using their proprietary enzyme hydrolysis and fermentation techniques on wheat straw feedstock.
    - BCI is building a commercial demonstration plant in Jennings, LA, US. The unique aspect of this company's technology is the genetically modified organism based on an E. coli bacterium with the ethanol production genes of zymomonas spliced into it. The process is claimed to be ideally suited to handle biomass feedstocks that produce both C_5 and C_6 sugars upon hydrolysis
- In China, Dynamotive Energy Systems is set to support the development of a pyrolysis plant in Henan province, China. The plant will be based of the company’s fast pyrolysis technology
- Pyrolysis technology is also used in other APEC member economies such as, Canada, Malaysia and the US. In Malaysia, The Genting Group produced Malaysia’s first commercially produced bio-oil from empty palm fruit bunches

- Neste Oil has built an 800 thousand ton per year renewable diesel plant in Singapore based on its NExBTL technology. It is the largest facility worldwide for producing diesel from renewable sources including a broad variety of natural oils and fats. The new plant in Singapore will provide this APEC member economy an opportunity to develop into a center for Asian biofuel production
- Both first and second generation feedstocks are mostly available in APEC member economies. However, second generation feedstocks, such as cellulosic biomass, should especially be considered for use by APEC member economies in biorefinery applications as these feedstocks are garnering the most attention
- A large number of other biomass gasification technologies have been proposed and are being developed worldwide, in Europe, Scandinavia, North America, Brazil, India, China, and elsewhere in Asia and in the world. Many of these are too small in scale, too weakly sponsored, are air-blown, or are so focused on power and heat production as to exclude them as candidates to commercially produce syngas for biofuels production in the mid-term
- Most APEC member economies fall in regions that do not have a problem with water resources. Member economies such as Peru and Viet Nam have physical water resources but lack the financial capability to develop infrastructure to properly distribute the water supply. Some areas of northern China and mid-west US have limited water supplies.
- Overall, however, APEC member economies are in a good position in terms of actual water supply resource based on a very macro economy view

As discussed in the report above, novel and innovative feedstocks for biofuels production are finding more attention in recent times, and are the subject of substantial investment and research. These investments and research are in turn being driven by the global demand for novel feedstocks with the most desirable qualities.

Key findings in regards to feedstock for biofuels production include:

- Though corn and sugarcane are still the predominant feedstocks for ethanol production as soy and palm oils are for the biodiesel industry, in the coming decades, this may not be the case. These food feedstocks may be replaced in the future with non-food competing feedstocks
- Non-food competing feedstocks are being sought and developed throughout the world and are in high demand as some economies will only approve biofuels projects that do not compete with food
- Many novel feedstocks for biofuel production are being investigated and used as alternatives to the traditional corn and sugarcane for ethanol and soy and palm oils for biodiesel
    - Key novel feedstocks being pursued for ethanol production include cassava, sorghum, waste cellulosics, and energy crops grown for cellulosic biomass such as misanthicus and switchgrass
    - Key novel feedstocks being pursued for biodiesel production include jatropha, algae, and waste oils.

- Jatropha is being widely pursued around the world and is receiving much attention. This has lead it to be poised to become a major feedstock to the global biodiesel industry
- Due to the sheer amount of resources available, research into waste cellulosics conversion may also create a paradigm shift when these technologies become commercially available
- Advances in feedstock development are being driven by sustainability, the food vs. fuel debate, land use, and climate change.
- Though not commercially viable yet, it is expected that should some of these feedstocks become commercially viable they will revolutionize the global biofuels market, and the global biofuels industry as a whole
- Advances in yield, disease resistance, and growth requirements are being researched in order to decrease farming costs and increase revenues

As discussed in the report above, biofuel co-products are an integral part of biofuels production.

Key findings in regards to co-products of biofuels production include:

- Biofuel co-products can be sold for a variety of end uses including:
  - Glycerin as a substitute ingredient for personal care products
  - DDGS as cattle feed
  - Syngas as a feedstock for chemical production
  - Carbon dioxide as a method of food preservation
  - Biochar as a fertilizer to enrich carbon content in soil
- Despite their many end uses, biofuel co-products run the risk of being oversupplied to their markets with increased biofuel production
- Without an end market to sell to, co-products can become more energy intensive and expensive to dispose of
- Concerns of this co-product supply/demand balance are realized and efforts are being made to ensure market demand for these co-products

Findings in respect to APEC member economies based on workshop presentations and discussion:

- Availability of non-food feedstocks and cost-effective cultivation system should be studied for bio-refinery technologies.
- Jatropha is a promising feedstock. However, there are many Jatropha species and it is important to choose the right species and then to isolate it to prevent contamination, which can have the effect of changing the species. Although Jatropha can grow in arid regions, water is very helpful for the yield. India and China are doing a lot of research concerning.

- Ethanol from corn requires large amounts of water for irrigation. In the US the corn-ethanol plants have reduced water use from 6: 1 to 3: 1. Bio-fuels produced from bio-refinery technologies can further reduce the water requirement by moving from corn to cellulosic crops that require less water.

- There is still a great deal of studies required on the bio-refinery technologies. Cost-effective bio-refinery processes and products should be studied and evaluated; however, the technologies used should consume energy efficiently and generates no additional environmental impact.
- Biofuels can be produced sustainably via fast pyrolysis technology for the application of boiler. After catalytic upgrading, biofuels can be further converted into 'green' gasoline, diesel, and jet fuel.
- To reduce bio-hydrogen cost from fermentation, it is not only the cost of hydrogen production but it is also essential to reduce the cost of wastewater treatment in order to make bio-hydrogen commercially viable.
- Distribution, retailing and vehicle compatibility of biofuels from bio-refinery processes should be evaluated.
- Life Cycle Analysis is needed to measure the opportunity for bio-refinery technologies, although it does depend on the assumptions made and the allocation of co-products. It is the trend in the US and globally.
- Government incentives and supports are needed for biofuels production and trade in the APEC region. There is a danger when governments intervene with incentives and mandates, but the reality is that government has its own reasons for wanting to drive alternative fuels and so they need to encourage them.

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Asia-Pacific Economic Cooperation

Bureau of Energy, Ministry of Economic Affairs

ITRI Industrial Technology Research Institute

AGENDA

APEC Workshop on Implications of Bio-refineries for Energy and Trade in the APEC Region

7-9 October 2009, Chinese Taipei

Organized by

Chinese Taipei:

Bureau of Energy, Ministry of Economic Affairs (BOE)
Industrial Technology Research Institute (ITRI)

Venue: B2, The Howard Plaza Hotel Taipei, Chinese Taipei

Wednesday, 7 October

08:30-09:00	**Registration**
09:00-09:15	**Welcome Remarks** ▪ The Bureau of Energy, Ministry of Economic Affairs, Chinese Taipei
09:15-09:30	**Opening Remarks** ▪ Dr. Cary Bloyd, Chairman of APEC Expert Group on New and Renewable Energy Technology (EGNRET)
09:30-10:15	**Keynote Speech – Overview of Bio-refinery Technologies (I)** ▪ Dr. Larry Song, General Manager, Nexant China, United States
10:15-10:45	Refreshment Break
10:45-11:30	**Keynote Speech – Overview of Bio-refinery Technologies (II)** ▪ Dr. Larry Song, General Manager, Nexant China, United States
11:30-12:15	**Development of Bio-Hydrogen Technologies in ITRI** ▪ Dr. Ming-Der Bai, Researcher, Energy and Environment Research Laboratories, Industrial Technology Research Institute, Chinese Taipei
12:15-13:45	Lunch
13:45-14:30	**Overview and Perspective of Bio-refinery Technologies in Thailand** ▪ Ms. Peesamai Jenvanitpanjakul, Former Deputy Governor (R&D), Sustainable Development, Thailand Institute of Scientific and Technological Research, Thailand
14:30-15:15	**Overview and Perspective of Bio-refinery Technologies in United States** ▪ Dr. Michael Wang, Group Manager, Argonne National Laboratory, United States

15:15-15:45	Refreshment Break
15:45-16:30	**Sustainable Biofuels from Fast Pyrolysis** ▪ Mr. Mark Reno, Managing Director , Envergent Technologies LLC, United States
16:30-16:50	**Biorefining, An Overview of Canadian Activities and Programs** ▪ Mr. Mark Stumborg, Head of Applied Science , Agriculture and Agri-Food Canada, Canada
18:00-20:00	**Welcome Reception (by invitation)**

Thursday, 8 October

09:00-09:45	**Opportunity for Bio-renewables in Oil Refinery** ▪ Dr. Sharry Lynch, Manager, Universal Oil Products, United States
09:45-10:30	**Algal Biofuels and Other Biorefinery Technologies in Australia** ▪ Dr. Peer Schenk, Program Leader, The University of Queensland, Australia
10:30-11:00	Refreshment Break
11:00-11:45	**Current Status of Biorefinery Technologies in Japan and Upgrading Technologies of Biofuels** ▪ Dr. Makoto Toba, Researcher, National Institute of Advanced Industrial Science and Technology, Japan
11:45-13:00	Lunch
13:00-13:45	**Guidelines for the Production and Introduction of Biofuels as Transport Fuels in APEC Economies** ▪ Dr. David Natusch, Managing Director, Resource Development Limited, New Zealand
13:45-14:15	**Development of PV Industry and Promotion Programs in Chinese Taipei** ▪ Dr. Jeong-Shein Chen, Division Director, Photovoltaics Technology Center, Industrial Technology Research Institute, Chinese Taipei.
14:15-15:00	Refreshment Break
15:00-17:00	**Roundtable Discussion on Implications of Bio-refineries for Energy and Trade in the APEC Region**
17:00	**Closing Remark** ▪ Energy & Environment Research Laboratories, Industrial Technology Research Institute, Chinese Taipei

Friday, 9 October

Site Visit to World Game 2009 Photovoltaic Facility (by Invitation)

08:00-08:42	The Howard Plaza Hotel -> Taipei MRT -> Taipei HSR Station(8:42)
08:42-10:18	High Speed Rail Train
10:18-10:35	Kaohsiung HSR Station -> World Game 2009 (by bus)
10:35-12:30	World Game 2009 – 1 MW PV
12:30-13:00	Lunch
13:00-15:00	World Game 2009 -> Formosa Boulevard MRT Station
15:00-15:36	Formosa Boulevard MRT Station -> Kaohsiung HSR Station(15:36)
15:36-17:16	Kaohsiung HSR Station -> Taoyuan HSR Station (Shuttle to Taoyuan Airport)
17:16- 18:00	Taoyuan HSR Station -> Taipei HSR Station -> Taipei MRT -> The Howard Hotel

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