FLOWSERVE

Technical Bulletin

Pumps for the Production of Renewable Fuels

Experience In Motion

Pumps for the Production of Renewable Fuels

Introduction

The 21st century "gold rush" is on to exploit the alternative or renewable energy, fuels and chemicals markets. How Flowserve responds over the next few years will determine if it will be a significant participant. This developing industry is researching and experimenting with many technology routes to successful commercialization. There are fortunes to be won or lost. Game-changing decisions will be made, much like those that confronted the early 20th century power pioneers in choosing between Edison's direct current electricity versus Westinghouse's alternating current format. Flowserve must be in a position to choose wisely.

As odd as it may seem, the ethanol and biodiesel industry has already matured. And for a variety of economic, political and social reasons, it may soon be in decline. What will take its place? How will the industry evolve?

At the far end of the spectrum is the "holy grail" of biofuels – hydrocarbons made by gasification of cellulosic biomass or by fermentation of sugars from biomass. But these processes are likely to be at least a decade away from true commercialization. Industry analysts foresee the production of biobutanol and cellulosic ethanol as the bridges between crop-based ethanol and biomass-based fuels.

The development of biobutanol and cellulosic ethanol is also a bridge to the realization of the biorefinery concept. Biotechnology visionaries anticipate large-scale integrated production of fuels, power and chemicals from biomass. In many ways, the biorefinery will be analogous to a petroleum refinery which produces multiple fuels and products from petroleum.

Flowserve has the capability to be a meaningful competitor as the biofuels and chemicals industry moves to more advanced and challenging process technologies. Many of its customers – E & C firms, process licensors and energy, chemicals and agricultural companies – are investing heavily in the development of biobutanol, cellulosic ethanol and the biorefinery fuels and chemicals concept. As the sophistication and scale of biofuels/chemicals production increase so do Flowserve's opportunities improve to exploit this emerging market segment.

Renewable Fuels and Chemicals Simplified

Trying to get a handle on the renewable fuels and chemicals market can be daunting… even mind numbing. For example, what are the processes used in biomass conversion? Is it primarily a heat source or an energy source? Or is it a biorefinery feedstock for conversion into fuels and chemicals? Is it all three? And what are the different processing routes in producing ethanol, biodiesel, biobutanol, cellulosic ethanol, etc.?

The diagram in Figure 1 was published by the European Biomass Industry Association (EUBIA) in 2006. It should be helpful in framing the variety of feedstocks, conversion processes and downstream products associated with biomass.

The table in Figure 2 is an attempt by the authors of this report to provide a rudimentary understanding of the categories, processes and downstream products associated with biofuels production.

Figure 1 – Feedstocks, Conversion Processes and Downstream Products Associated With Biomass
Source: EUBIA
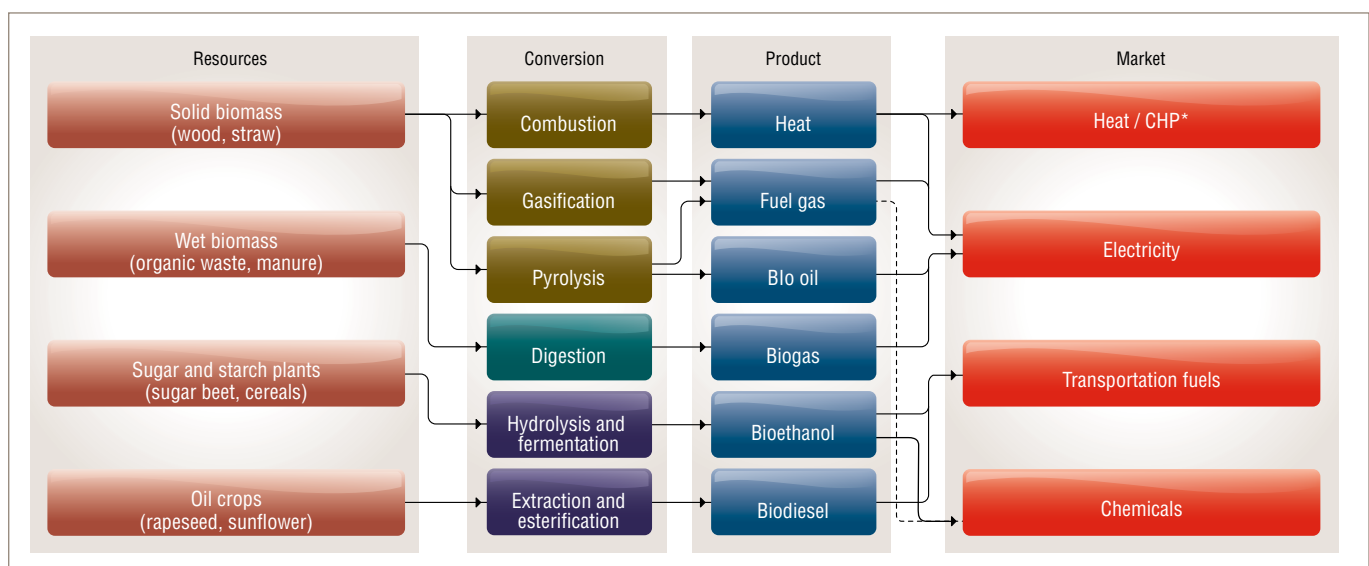
*CHP – Combined Heat and Power

Figure 2 – Renewable Fuels and Chemicals

Category	Bioethanol	Biodiesel	Biobutanol	Cellulosic Ethanol	Biomass Refinery
Feedstock	Corn, maze, sugar beet, sugar cane	Virgin vegetable oils, animal fats, spent cooking oils and trap grease	Engineered energy crops, cellulosic materials, wood residues	Agricultural wastes, wood residues, selected municipal waste	Engineered energy crops, agricultural and food processing wastes, wood residues, pulp and paper mill sludge, livestock waste, selected municipal waste
Process	Fermentation with yeast	Transesterification – Base catalyzed – Acid catalyzed	• ABE fermentation • BA101 fermentation • Guebet catalysis • 2-stage fermentation • Gasification • Digestion – Aerobic – Anaerobic	• Celluloses – Acid or enzymatic hydrolysis – Fermentation with yeast • Gasification – Synthesis gas – Microbial fermentation or chemical catalysts	• Fermentation (yeast) • Digestion (bacteria) • Gasification
Products	Ethanol CO_2 Distiller grain Chemical	Biodiesel Glycerine Chemical	Biobutanol Chemical Pharmaceutical Nutraceutical	Ethanol Chemical Lignin Lignin (heat source)	Fuels (biodiesel, ethanol, methane, BTL*, DME**) Chemicals/materials Electricity

Note:
There are four basic categories of biomass (including agricultural crops) conversion.
They are:
1. Direct combustion
2. Thermochemical (pyrolysis, gasification, liquefaction)
3. Biochemical (hydrolysis, aerobic and anaerobic digestion, fermentation)
4. Physiochemical (extraction and transesterification)

* Biomass to liquid fuel (BTL)
** Dimethylether (DME)

Section 1: Ethanol

Background

With volatile gasoline prices and geopolitical issues driving some countries to reduce their dependency on oil, renewable fuels are becoming increasingly attractive. And, no other renewable fuel has received as much attention as ethanol.

Some hail ethanol, which can be produced from plants such as corn, wheat, barley and sugarcane, as a panacea for global energy problems. Others see ethanol production as a relatively safe business opportunity as it is heavily subsidized by governmental tax policies.

The reality is complex. Though still a tiny industry compared to gasoline, ethanol could become a more prominent part of the European, North American and global fuel supply in coming years.

Ethanol is derived from plants through a fairly straightforward process. In one common method corn is first ground into a fine powder, mixed with water and then heated. An enzyme is then added to convert the mixture into sugars before yeast is added to ferment it. The resulting liquid, called "beer," is about 10% alcohol. A distillation process then separates the alcohol from the rest of the mixture before the remaining water is removed. The result is essentially pure alcohol. A small amount of gasoline is added to render the liquid undrinkable. Then the fuel can be used by itself or as a supplement to gasoline to power automotive vehicles.

Brazil is often seen as a model in the ethanol sector. Since the 1970s ethanol has replaced about 800 million barrels of oil, the equivalent of almost two years of current Brazilian oil production. In effect, Brazil has achieved oil self-sufficiency with the help of ethanol production.

In South America, India and other warm climates, sugarcane and sugar beets provide the feedstock for ethanol production. In North America and Europe, corn is the primary feedstock while rice is prominent in South Asia.

In virtually all cases renewable fuels production is being required and subsidized by a country's central government. For example, in the United States the Energy Policy Act of 2005 (EPACT) is the driving force. In Europe it is EU Directive 2003/30/EC.

Ethanol Defined

Hawley's Condensed Chemical Dictionary defines ethanol as follows:

Ethyl Alcohol

(alcohol; grain alcohol; ethanol; EtOH).
CAS: 64-017-5, C_2H_5OH.

Properties

(Pure 100% absolute alcohol, dehydrated) Colorless, limpid, volatile liquid; ethereal vinous odor; pungent taste. Bp 78.3°C, fp – 117.3°C, refr index 1.3651 (15°C), surface tension 22.3 dynes/cm (20°C), viscosity 0.0141 cP (20°C), vap press 43 mm Hg (20°C), specific heat 0.618 cal/g K (23°C), flash p 55°F (12.7°C), d 0.816 (15.56°C), bp 78°C, fp – 114°C, autoign temp 793°F (422C). Miscible with water, methanol, ether, chloroform and acetone (95% alcohol).

Ethanol Process Explained

This report is focused on ethanol production from corn. Although the production processes may vary by region and feedstock, they are all technically demanding applications that include solids-handling, corrosive and erosive environments. The production of ethanol or ethyl alcohol from starch or sugar-based feedstocks is among man's earliest ventures into value-added processing. While the basic steps remain the same, the process has been considerably refined in recent years, leading to a very efficient process. There are two production processes: wet milling and dry milling. The main difference between the two is in the initial treatment of the grain. As of January 2007, dry mill facilities account for 82% of ethanol production and wet mills 18% in North America.

The Dry Milling Process

In dry milling, the entire corn kernel or other starchy grain is first ground into flour, which is referred to in the industry as "meal" and processed without separating out the various component parts of the grain. The meal is slurried with water to form a "mash." Enzymes are added to the mash to convert the starch to dextrose, a simple sugar. Ammonia is added for pH control and as a nutrient to the yeast.

The mash is processed in a high-temperature cooker to reduce bacteria levels ahead of fermentation. The mash is cooled and transferred to fermenters where yeast is added and the conversion of sugar to ethanol and carbon dioxide (CO_2) begins.

The fermentation process generally takes about 40 to 50 hours. During this part of the process, the mash is agitated and kept cool to facilitate the activity of the yeast. After fermentation, the resulting "beer" is transferred to distillation columns where the ethanol is separated from the remaining "stillage." The ethanol is concentrated

to 190 proof using conventional distillation and then is dehydrated to approximately 200 proof in a molecular sieve system.

The anhydrous ethanol is then blended with about 5% denaturant (such as natural gasoline) to render it undrinkable and thus not subject to beverage alcohol tax. It is then ready for shipment to gasoline terminals or retailers.

The stillage is sent through a centrifuge that separates the coarse grain from the solubles. The solubles are then concentrated to about 30% solids by evaporation, resulting in Condensed Distillers Solubles (CDS) or "syrup." The coarse grain and the syrup are then dried together to produce dried distillers grains with solubles (DDGS), a high-quality, nutritious livestock feed. The CO_2 released during fermentation is captured and sold for use in carbonating soft drinks and beverages and the manufacture of dry ice.

Figure 3 – Typical Dry Milling Process
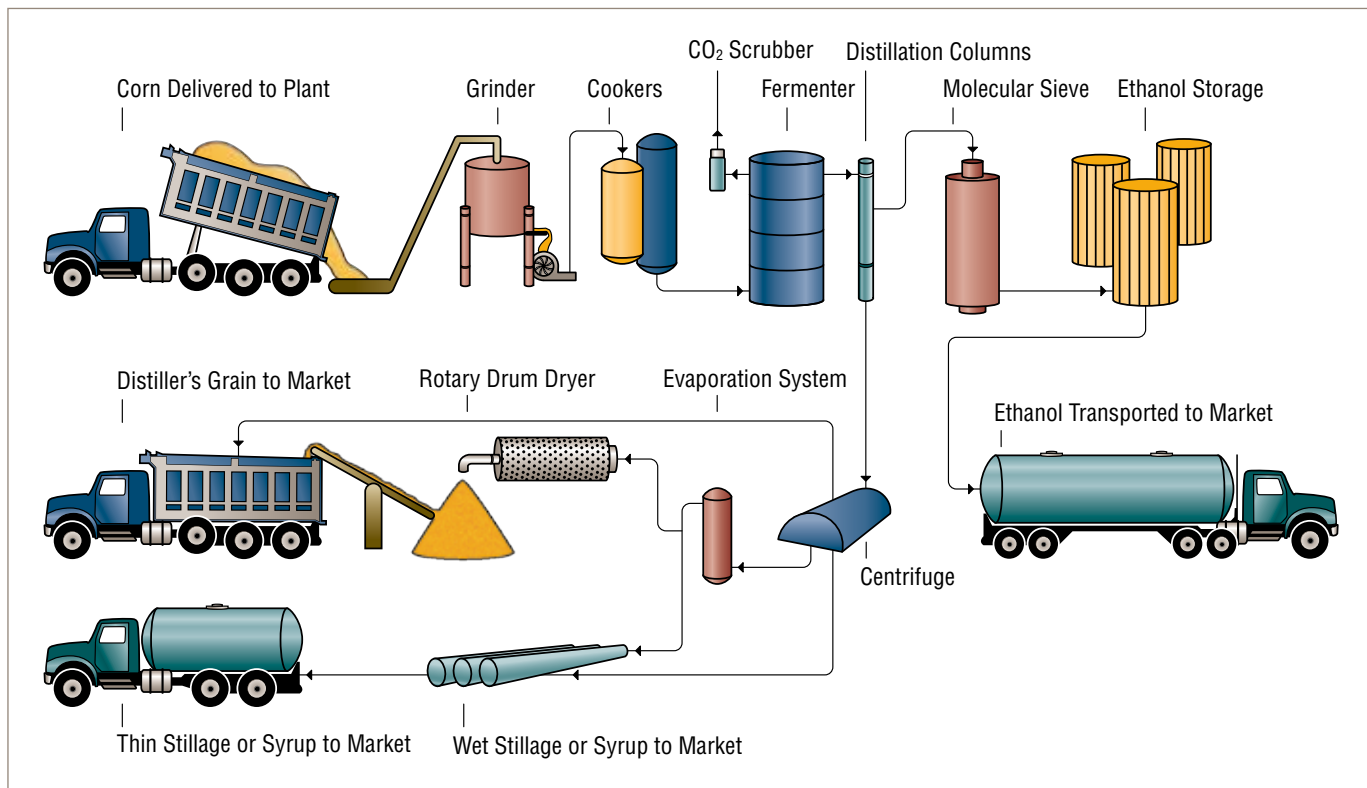
The Wet Milling Process

In wet milling, the grain is soaked or "steeped" in water and dilute sulfurous acid for 24 to 48 hours. This steeping facilitates the separation of the grain into its many component parts.

After steeping, the corn slurry is processed through a series of grinders to separate the corn germ. The corn oil from the germ is either extracted on-site or sold to crushers who extract the corn oil. The remaining fiber, gluten and starch components are further segregated using centrifugal, screen and hydroclonic separators.

The steeping liquor is concentrated in an evaporator. This concentrated product, heavy steep water, is co-dried with the fiber component and is then sold as corn gluten feed to the livestock industry. Heavy steep water is also sold by itself as a feed ingredient and is used as a component in Ice Ban®, an environmentally friendly alternative to salt for removing ice from roads.

The gluten component (protein) is filtered and dried to produce the corn gluten meal co-product. This product is highly sought after as a feed ingredient in poultry broiler operations. The starch and any remaining water from the mash can then be processed in one of three ways: fermented into ethanol, dried and sold as dried or modified corn starch, or processed into corn syrup. The fermentation process for ethanol is very similar to the dry mill process described previously.

Regardless of the milling process chosen, approximately 2.8 gallons (10 liters) of ethanol are produced from one bushel (35 liters) of corn. While much of the corn turns into ethanol, some of the corn also yields by-products such as distillers dried grains with solubles (DDGs) that can be used to fulfill a portion of the diet of livestock. A bushel of corn produces about 18 lb (8.2 kg) of DDGs.

For use as a fuel, the ethanol must first be purified. Fractional distillation can concentrate ethanol to 95.6% (89.5 mole %) by weight. The mixture of 95.6% ethanol and 4.4% water by weight is an azeotrope with a boiling point of approximately 172°F (78°C) and cannot be further purified by distillation. Therefore, 95% ethanol in water is a fairly common solvent.

Figure 4 – Typical Wet Milling Process
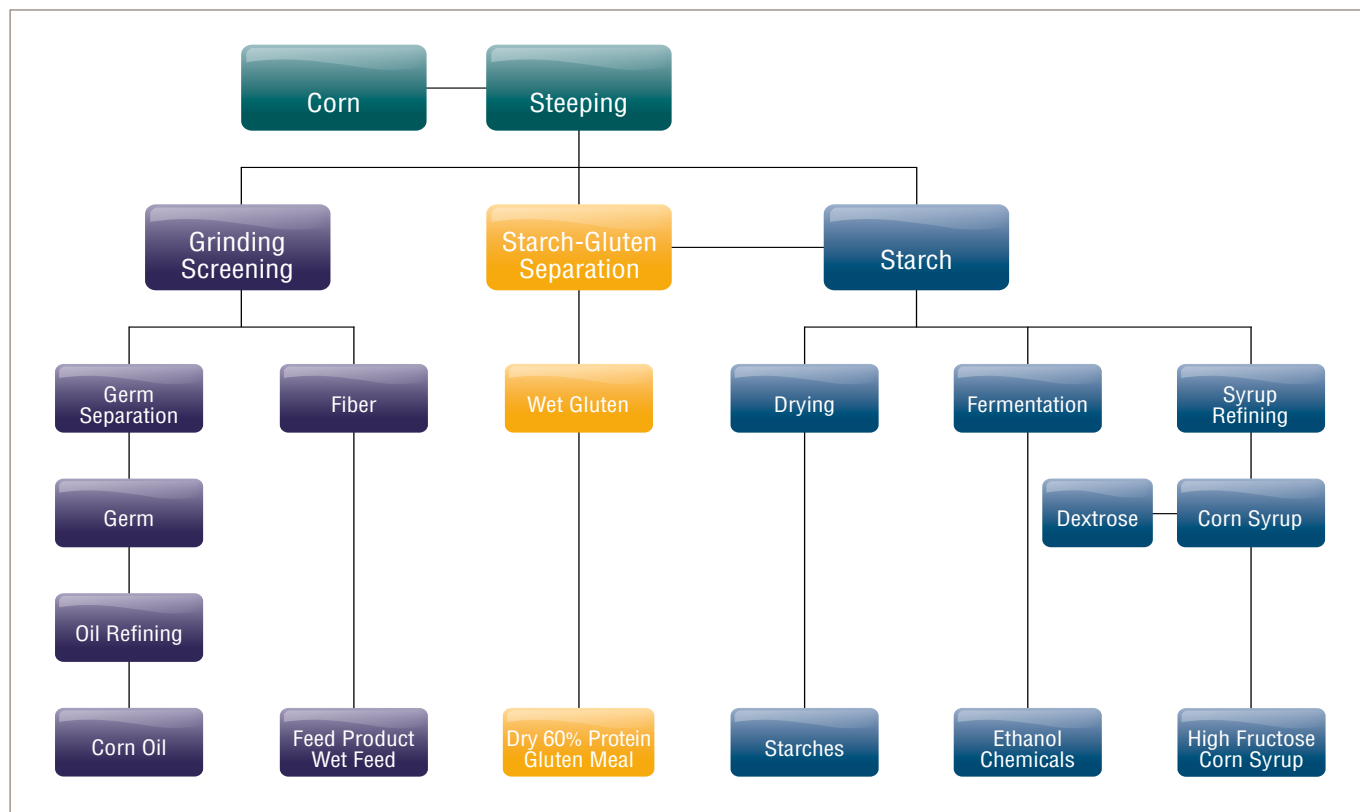
®Ice Ban is a registered trademark of North American Patent Holdings, Inc.

A Closer Look at the Dry Milling Process

There are basically eight steps in the dry mill ethanol process.

1. **Milling:** The corn (or barley or wheat) will first pass through hammer mills, which grind it into a fine powder called meal.

2. **Liquefaction:** The meal will then be mixed with water and the primary enzyme (alpha-amylase), and will pass through cookers where the starch is liquefied. Heat will be applied at this stage to enable liquefaction. Cookers with a high-temperature stage 250° - 300°F (120° - 150°C) and a lower temperature holding period 205°F (95°C) will be used. These high temperatures reduce bacteria levels in the mash.

3. **Saccharification:** The mash from the cookers will then be cooled and the secondary enzyme (gluco-amylase) will be added to convert the liquefied starch to fermentable sugars (dextrose), a process called saccharification.

4. **Fermentation:** Yeast will then be added to the mash to ferment the sugars to ethanol and carbon dioxide. Using a continuous process, the fermenting mash will be allowed to flow, or cascade, through several fermenters until the mash is fully fermented and then leaves the final tank. In a batch fermentation process, the mash stays in one fermenter for about 48 hours before the distillation process is started.

5. **Distillation:** The fermented mash, now called "beer," will contain about 10% alcohol, as well as all the non-fermentable solids from the corn and the yeast cells. The mash will then be pumped to the continuous flow, multi-column distillation system where the alcohol will be removed from the solids and the water. The alcohol will leave the top of the final column at about 96% strength, and the residue mash, called stillage, will be transferred from the base of the column to the co-product processing area.

6. **Dehydration:** The alcohol from the top of the column will then pass through a dehydration system where the remaining water will be removed. Most ethanol plants use a molecular sieve to capture the last bit of water in the ethanol. The alcohol product at this stage is called anhydrous (pure, without water) ethanol and is approximately 200 proof.

7. **Denaturing:** Ethanol that will be used for fuel is then denatured with a small amount (2-5%) of some product, like gasoline, to make it unfit for human consumption and non-taxable.

Figure 5 – Details of the Dry Milling Process
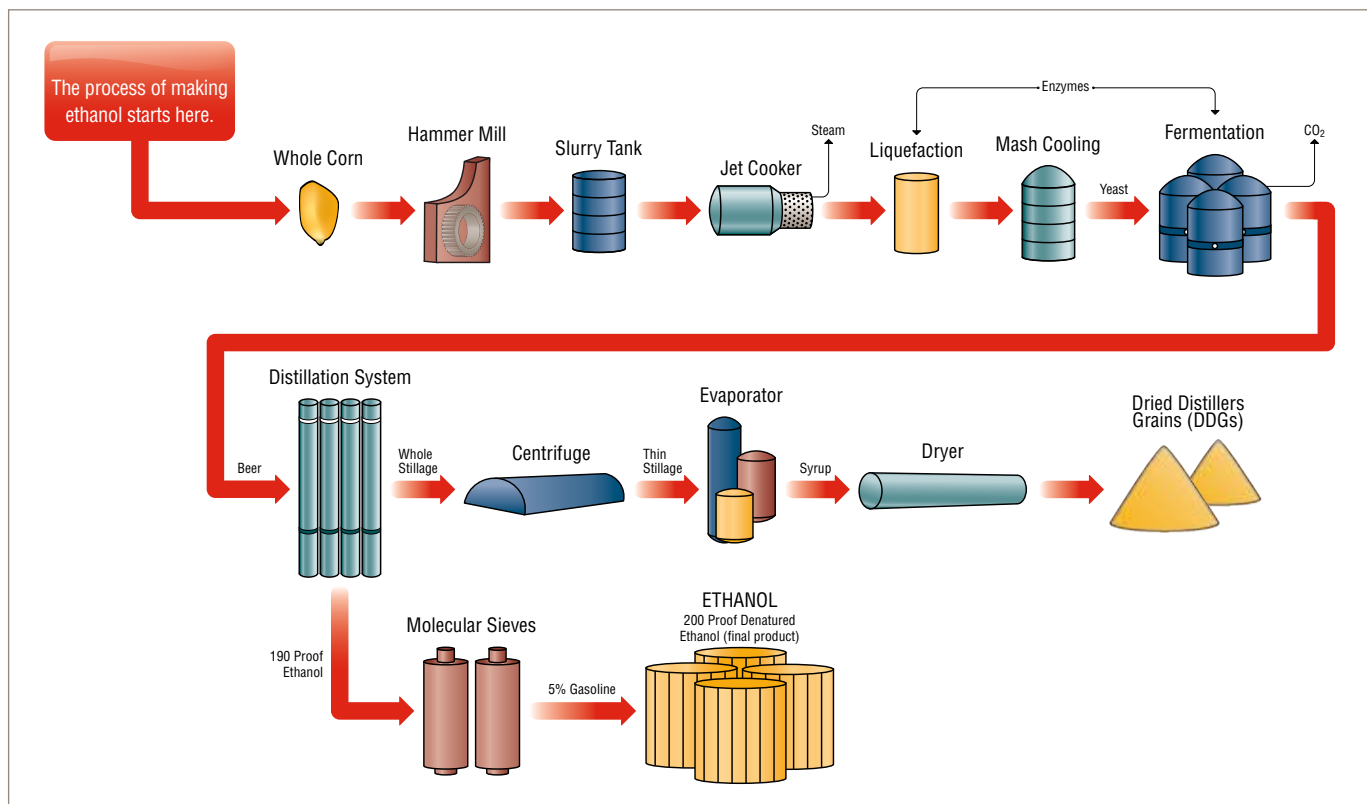
Figure 6 – Dry Milling Process Flow Diagram
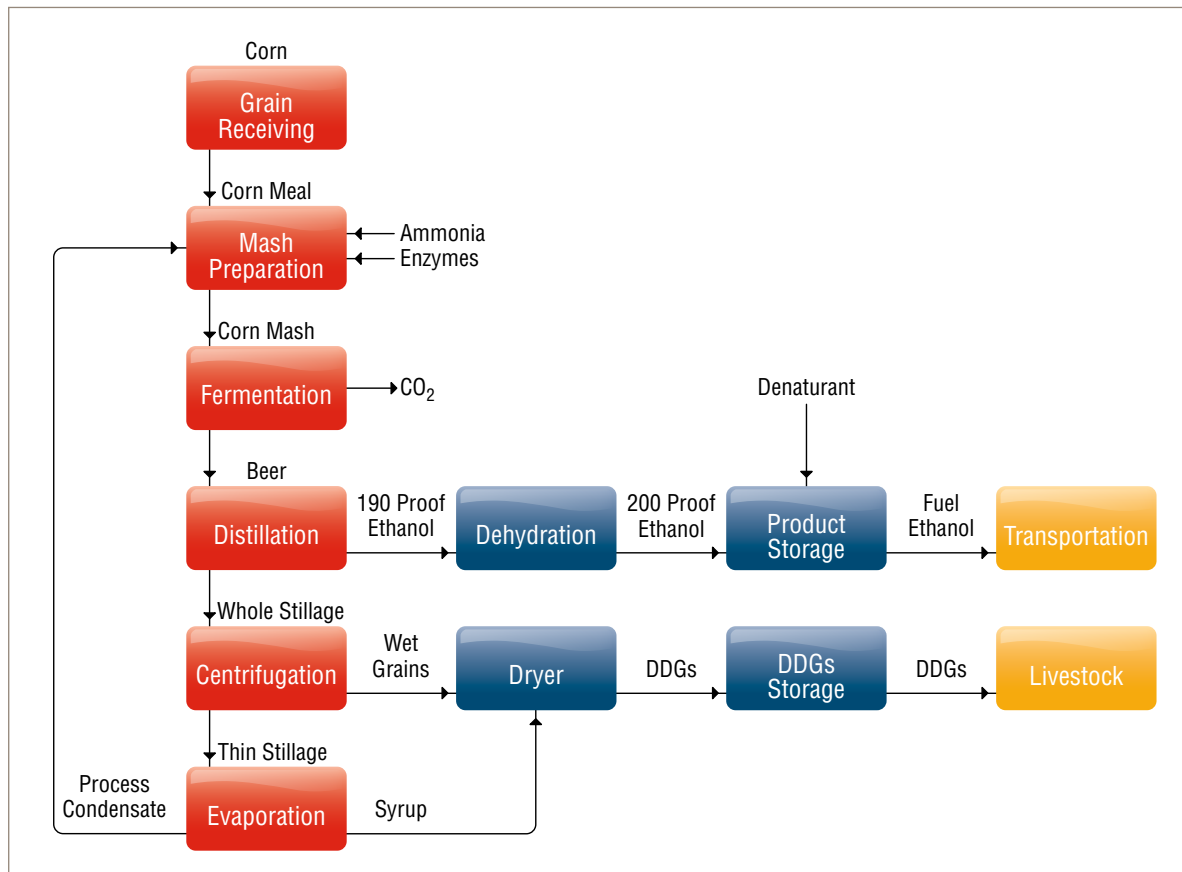
8. **Co-Products:** There are two main co-products created in the production of ethanol: carbon dioxide and distillers grain. Carbon dioxide is given off in great quantities during fermentation and many ethanol plants collect that carbon dioxide, clean it of any residual alcohol, compress it and sell it for use to carbonated beverages or in the flash freezing of meat. Distillers grains, wet and dried, are high in protein and other nutrients and are a highly valued livestock feed ingredient. Some ethanol plants also create a "syrup" containing some of the solids that can be sold as a separate product in addition to the distillers grain or combined with it. Ethanol production is a no-waste process that adds value to the corn by converting it into more valuable products.

Notes

1. Ethanol is produced by the addition of enzymes to the pure starch slurry to hydrolyze the starch to fermentable sugars. Following hydrolysis, yeast is added to initiate the fermentation process.

2. Hydrolysis is a chemical reaction in which water reacts with another substance to form two or more new substances. Examples are: conversion of starch to glucose in the presence of suitable catalysts; and conversion of sucrose (cane sugar) to glucose and fructose by reaction with water in the presence of an enzyme or acid catalyst.

Pumping Ethanol

Typical Pump Applications

Ethanol production presents a difficult pumping environment, including solids-handling to 30%, corrosive caustics and erosive liquids. Applications include:

- Mash pumps
  – 20-30% solids; temp from 95° to 185°F (35° to 85°C); visc 5-30 cP; sp gr 1.2; pH 2-4
- Fermentation/beer pumps
  – 20% solids; tem from 95° to 130°F (35° to 55°C); visc 1.0 cP; sp gr 1.2; pH 4.0
- Evaporation pumps
  – 15-20% solids; temp to 210°F (100°C); visc 1.0 cP; sp gr 1.2; pH 4.0
- Process condensate
  – temp to 185°F (85°C); visc 1.0 cP; sp gr 1.0, pH 4.5
- Beer bottoms pumps
  – 20-30% solids (including syrup); temp 100° to 120°F (38° to 50°C); visc 350 cP; sp gr 1.15; pH 4.0
- Product pumps
  – temp to 95°F (35°C); visc 0.89 cP; sp gr 0.78; pH 7.0
- CIP pumps
  – 5-50% caustic acid; temp to 82°F (28°C); visc 0.46-5.0 cP; sp gr 1.04-1.56; pH 4-11

Auxillary Applications

- Chemical and ethanol unloading - storage - transfer
- Cooling water
- Waste water
- Boiler feed
- Fire fighting
- Slurry

Flowserve Pump Applications

Flowserve has a long history of success in the corn milling industry. Its Durco® Mark 3™ (ANSI B73.1) and Durco CPX3 (ISO 2858/5199) chemical process pumps and its FRBH stock pumps have proven their reliability and efficiency in this most difficult pumping environment.

In fact, the Durco range of pumps is extraordinarily versatile and may be applied in virtually all ethanol production services. Durco has become the standard pump of the corn milling and processing industry.

The FRBH heavy-duty paper and stock and process pump is excellent for slurry-handling service. Its options include a recessed impeller and an inducer. A high specific speed axial flow pumping device an inducer provides significant improvement in suction performance by reducing pump NPSHR.

Page 12 of this report details the Flowserve materials and engineering advantages in corn milling and ethanol production.

Before identifying the specific applications of Flowserve pumps, take a brief look at special and auxiliary services.

- **Chemical unloading/storage/transfer** - Sulfuric acid and caustic sodas to balance pH and for sanitation are very corrosive. Self-priming pumps are preferred. Flowserve offers:
  – Durco Mark 3 unitized self primer
  – Durco CPX3 self priming pump
- **Liquefaction** - To maintain a pH of 7 sulfuric acid or sodium hydroxide (caustic soda) is added to the process liquid.
  – Sulfuric Acid < 60°C (140°F)
    • Durco CPX3 standard ISO pump in Alloy 20 with double seals
    • Durco Mark 3 standard ANSI pump in Alloy 20 with double seals
  – Sodium hydroxide < 60°C (140°F)
    • Durco CPX3 standard ISO pump in duplex stainless steel with double seals
    • Durco Mark 3 standard ANSI pump in duplex stainless steel with double seals
- **Enzyme handling** - Enzyme fluids like alpha-amylase and gluco-amylase are very sticky and polymerize on the mechanical seal faces when exposed to air, causing failures.
  – Durco CPX3 standard ISO pump in 316 stainless steel with double seals
  – Durco Mark 3 standard ISO pump in 316 stainless steel with double seals
- **Cooling water** - Flowserve offers the VTP vertical turbine pump as well as the FRBH, LR and LNN axially split and single-stage pumps.
- **Sump pumps** - Flowserve offers:
  – CPXV vertical sump
  – MDX vertical submersible, formed stainless steel
- **Boiler feed pumps** - Flowserve offers:
  – WDX, NM and WXH radially split, multistage ring section pumps
  – LLR axially split two-stage

Ethanol Production Pumps

The following application and pump listing is representative of a high pressure rectification process system producing 946 250 L (250 000 g) of ethanol annually. Pump models are for Mark 3 and FRBH units.

Liquefaction	Model	Material	VFD
Slurry mix tank	10FRBH182-IND	CD4M	
Tank no. 1	3K10x8-16RV	CD4M	Yes
Tank no. 2 bypass	3K8x6-16ARV	CD4M	Yes
Tank no. 2	3K8x6-16ARV	CD4M	Yes
Mash booster	3K8x6-16ARV	CD4M	Yes
Beer booster	4FRBH182	CD4M	Yes

Fermentation

Figure 7 – Pumps for Fermentation
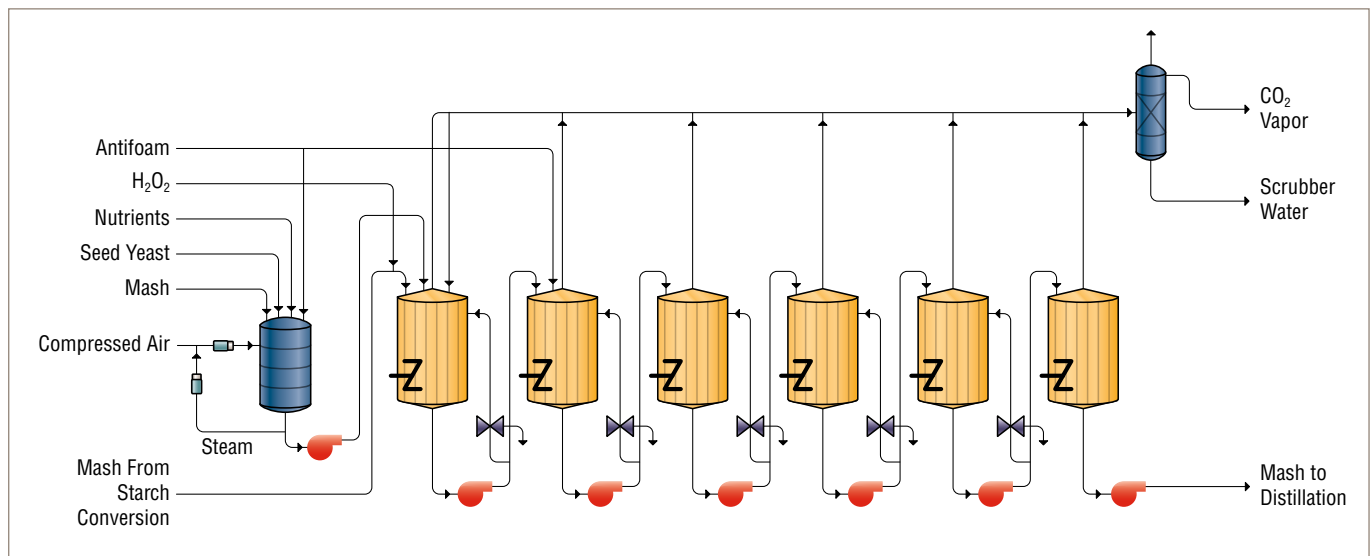
Fermentation	Model	Material	VFD
Fermenters nos. 1-8 (8)	3K10x8-16HRV	CD4M	
Primary scrubber	2K3x2-82RV	316SS	
Alcohol return	2K3x1.5-13RV	CD4M	
Beer feed A & B (2)	3K8x6-16ARV	CD4M	Yes
Fermenter CIP return nos. 1-4 (4)	2K4x3-10HRV	316SS	

Distillation

Figure 8 – Pumps for Distillation
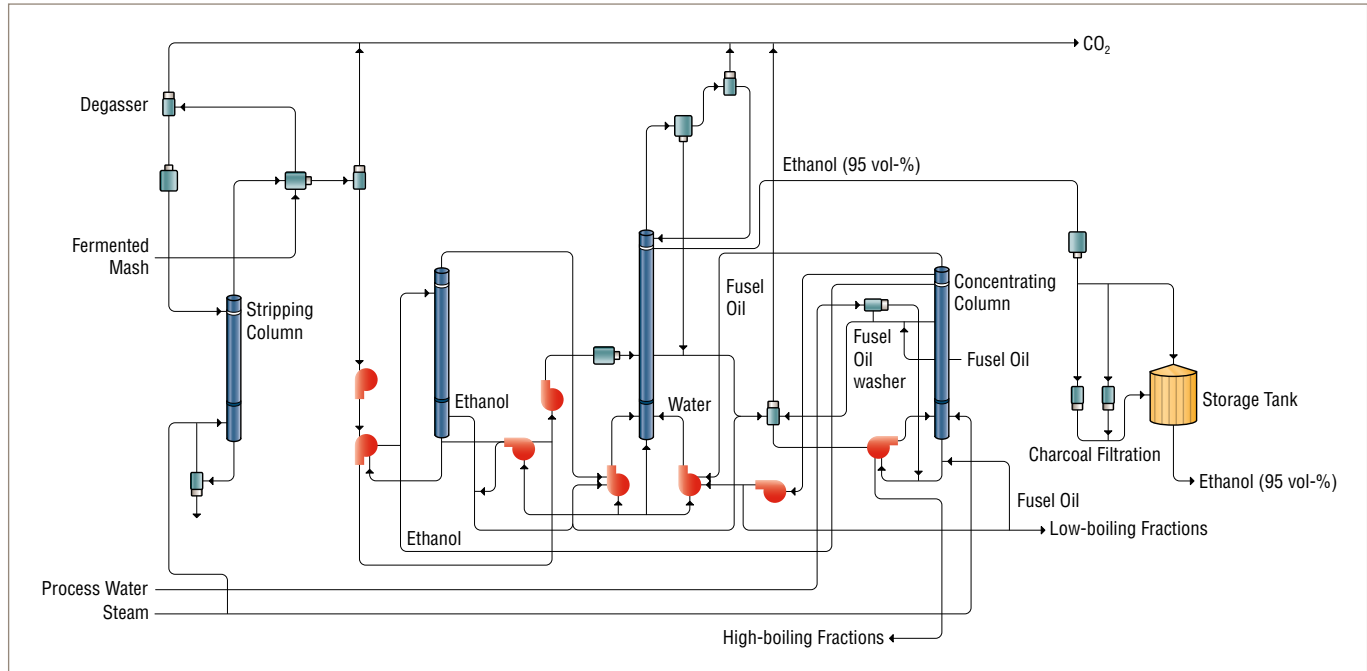
Distillation, Drying and Evaporation	Model	Material	VFD
Beer column no. 1 reboiler	8FRBH223-IND	CD4M	
Beer column no. 2 reboiler	8FRBH182-IND	CD4M	
Beer column no. 2 flash receiver	2K3x1.5-13RV	CD4M	
Beer column no. 1 bottoms	3FRBH182	CD4M	
Beer column no. 2 bottoms	2K6x4-13ARV	CD4M	
Rectifier column	2K3x2-10ARV	316SS	
Rectifier column feed	2K4x3-10RV	316SS	
Rectifier column reflux	2K4x3-10HRV	316SS	
Regeneration	2K6x4-10RV	316SS	Yes
Product	2K3x2-13RV	316SS	
Tr no.1 first effect evaporator	3K10x8-16HRV	CD4M	
Tr no. 1 second effect evaporator	3K10x8-16HRV	CD4M	
Tr no. 1 third effect evaporator	3K10x8-16HRV	CD4M	
Tr no. 1 evaporator condensate	2K4x3-10RV	316SS	
Tr no. 1 evaporator vacuum eductor	2K4x3-13RV	316SS	Yes
Tr no.1 second effect forward feed	2K4x3-13RV	CD4M	
Tr no. 1 finisher forward feed	2K3x1.5-10ARV	CD4M	
Tr no. 1 finisher recirc	12FRBH183-IND	CD4M	
Dryer exhaust condensate	1K1.5x1-82R	316SS	
Tr no. 2 first effect evaporator	3K10x8-16HRV	CD4M	
Tr no. 2 second effect evaporator	3K10x8-16HRV	CD4M	
Tr no 2 third effect evaporator	3K10x8-16HRV	CD4M	
Tr no. 2 evaporator condensate	2K4x3-10RV	316SS	
Tr no. 2 evaporator vacuum eductor	2K4x3-13RV	316SS	Yes
Tr no 2 second effect forward feed	2K3x2-13RV	CD4M	
Tr no. 2 finisher forward feed	2K3x1.5-10ARV	CD4M	
Tr no. 2 finisher recirc	12FRBH183-IND	CD4M	

Stillage Handling

Figure 9 – Pumps for Stillage Handling
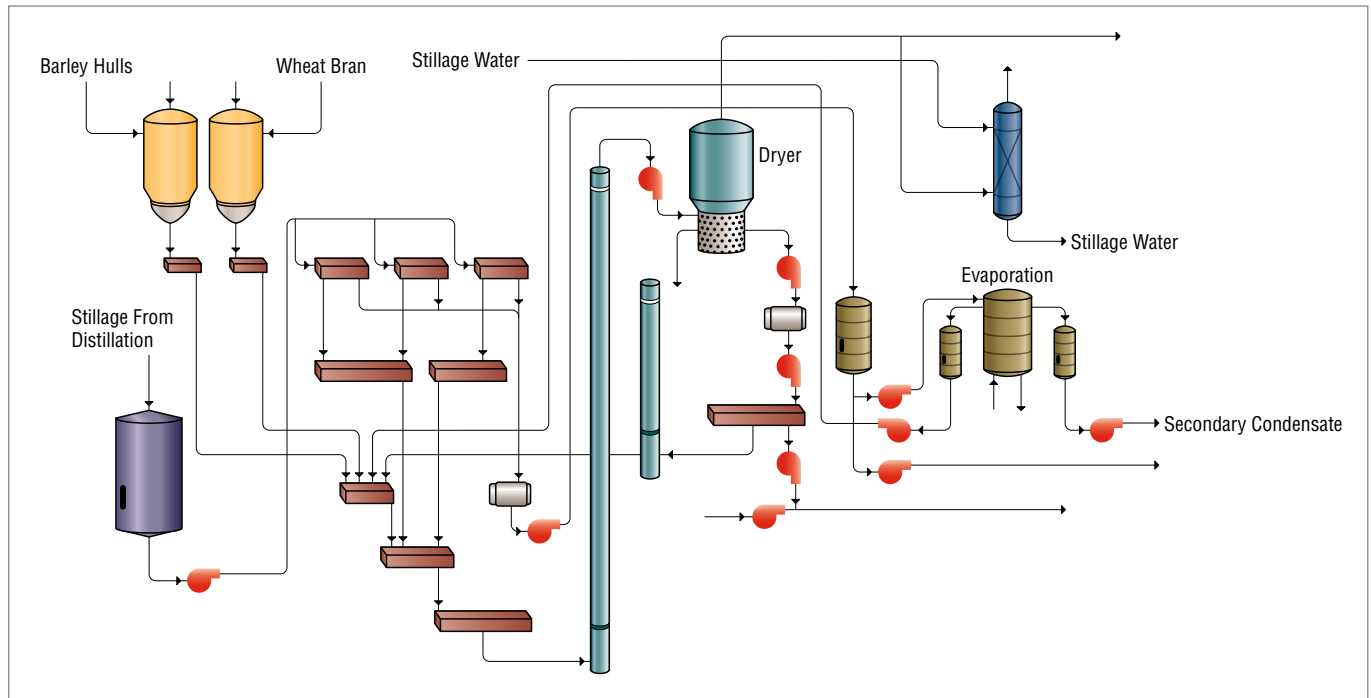
Stillage	Model	Material	VFD
Thin stillage transfer	3K8x6-14ARV	CD4M	
Whole stillage	3K8x6-14ARV	CD4M	
Thin stillage A & B (2)	3K8x6-14ARV	CD4M	
Syrup	3K8x6-14ARV	CD4M	
Ethanol	**Model**	**Material**	**VFD**
Denaturant truck loading A & B (2)	1K1.5x1LF-82	316SS	
Denaturant truck loading C	1K1.5x1LF-82	316SS	
Ethanol truck loading A & B (2)	2K4x3-82RV	316SS	
Ethanol truck loading C	2K4x3-82RV	316SS	
Ethanol transfer (3)	2K6x4-10RV	316SS	
Utility	**Model**	**Material**	**VFD**
Cooling water nos. 1-5 (5)	16FRBH244-IND	SSF	
Cooling water booster	2K4x3-10HRV	D/C	
Chilled water nos. 1-3 (3)	3K10x8-16HRV	CI	
Steam condensate no. 1	2K4x3-10RV	CI	
Steam condensate no. 2	2K3x1.5-13RV	CI	
Process condensate	3K8x6-14ARV	CD4M	

Flowserve Advantages

The Most Trusted in the Industry

Flowserve has been successfully providing equipment for the corn processing and ethanol production industry for more than 35 years. Its reputation has been built upon superior pump design, unequaled materials expertise and field-proven performance.

Ethanol Pumping Expertise

- Mash
- Evaporation
- Beer bottoms
- Final ethanol
- Acid wash
- Gasoline
- Boiler feed
- Fermentation/beer
- Process condensate
- Product
- CIP
- Cooling water
- Sump
- Milling/steeping

Superior Product Design

- With ideal design features for abrasive and corrosive services, Flowserve ANSI and ISO process pumps are the global workhorses of ethanol production
- Reverse vane impeller transfers erosion/corrosion from the casing to the less expensive rear cover; repeatable "as new" performance after wear and impeller adjustment; low NPSHR
- Tapered bore seal chamber with flow modifiers permits less costly sealing arrangement due to self-venting and solids-handling capabilities
- Heavy-duty ANSI 3A power end with lifetime warranty gives full protection during hose down
- Reinforced baseplate options
- All products comply with ATEX and are CE marked
- Industry specific repeller design available as an option

Materials Expertise

Many ethanol production pump users standardize on ASTM A995, grade CD4MCuN (DIN SEW 410) for performance and inventory cost reduction purposes. Invented by Flowserve, this duplex stainless steel has a hardness (224 Brinell) approximately three times that of austenitic stainless steels. It also has greater pitting and crevice corrosion resistance compared with other duplex stainless steels or 316SS.

- Other materials include:
- ASTM A995, grade CD4MCuN with hard coating
- CR29 hard chrome cast iron (>500 Brinell)
- ASTM A744, grade CN7M (Alloy 20) (WN 1.4500)
- ASTM A744, grade CF8M (316SS) (DIN 17445)
- ASTM A395, grade 60-40-18 (DCI)
- Fluoropolymer

In addition to standard shaft materials, Flowserve offers two highly corrosion- and abrasion-resistant proprietary alloys. These include:

- DC8, a cobalt-based alloy with appreciable amounts of chromium and molybdenum
- SD77 high silicon iron

Industry-Leading Ethanol Production Pumps

- 🟡 **Starch Conversion**
- 🔵 **Fermentation**
- 🟤 **Distillation**
- 🟣 **Storage**
- 🔷 **Stillage Handling**

Standard Process Pumps
Mark 3 (ANSI B73.1), CPX3 (ISO 2858/5199)
🟡🔵🟤🟣🔷 • Standard
🟡🔵⚪⚪🔷 • Recessed impeller
🟡🔵🟤🟣🔷 • Self-priming
🟡🔵🟤🟣🔷 • Dynamically sealed

Fluoropolymer Lined Pumps
🟡🔵⚪⚪⚪ • PolyChem™ S-Series (ANSI B73.1 and ISO 2858)

Heavy-duty (Stock) Pumps
🟡🔵🟤🟣🔷 • FRBH
🟡🔵🟤🟣🔷 • Mark 3, Group 3 and 4

Sealless Pumps
🟡🔵⚪🟣⚪ • Magnetic drive-metallic
    – Guardian® (ANSI B73.1)
    – CPX3S (ISO 2858/5199)
🟡🔵⚪⚪⚪ • Magnetic drive-fluoropolymer lined
    – PolyChem M-Series (ANSI B73.1 and ISO 2858)

Cooling Water and Sump Pumps
🟡⚪⚪⚪⚪ • VTP vertical turbine
🟡⚪⚪⚪⚪ • LR and LNN axially split, single-stage
🟡🔵🟤🟣🔷 • Standard and cantilever sump pumps
🟡⚪⚪⚪🔷 • MDX vertical submersible, formed SS

Boiler Feed Pumps
🟡⚪⚪⚪⚪ • Radially split, multistage ring section

CPXV

CPX3
Standard

Mark 3
Standard

PolyChem
M-Series

FRBH

LNN

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Specific Advantages of the Durco Mark 3 and Durco CPX3 Designs

Flowserve has been successful in the ethanol market primarily because of the inherent features and benefits of the design.
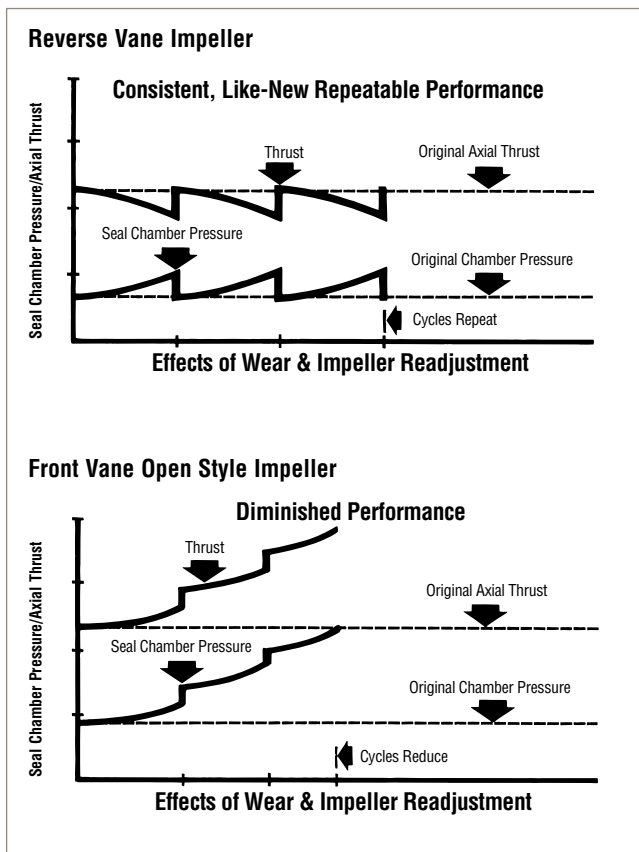
Reverse Vane Impeller (RV)

Unlike alternative front vane open style impellers, the RV impeller has only one set of pumping vanes and one critical tolerance between the impeller and rear cover. One setting establishes:

- Performance
- Efficiencies
- Seal chamber pressures (i.e., mechanical seal MTBPM)
- Thrust/axial loads (i.e., bearing life)

The front vane open style impeller has two sets of pump-out vanes and two critical tolerance locations. The front vane of the impeller clearance to the casing establishes performance and efficiencies. The impeller pump-out vanes to the rear cover establishes seal chamber pressures and seal life and thrust loads and bearing life.

Since an impeller can only be set in one direction, the RV impeller has inherent advantages.

Figure 10 – Impact of Impeller Design on Pump Performance

Reverse Vane Impeller

Consistent, Like-New Repeatable Performance

Seal Chamber Pressure/Axial Thrust

Thrust / Original Axial Thrust

Seal Chamber Pressure / Original Chamber Pressure

Cycles Repeat

Effects of Wear & Impeller Readjustment

Front Vane Open Style Impeller

Diminished Performance

Seal Chamber Pressure/Axial Thrust

Thrust / Original Axial Thrust

Seal Chamber Pressure / Original Chamber Pressure

Cycles Reduce

Effects of Wear & Impeller Readjustment

One Critical Tolerance

The RV design is unique in that it offers repeatable pump performance throughout the life of the pump. This is possible because the impeller clearance is set between the rear of the impeller and the rear cover, not the front of the impeller and the casing as with the front vane open style impeller. Since this clearance affects both the seal chamber pressure and the axial thrust, when you readjust the clearance, you are returning to the original values. Conversely, with a front open impeller design, clearance adjustment is toward the casing and both stuffing box pressures and axial thrust increase as the clearance between the impeller and cover increase.

True Back Pull-out Design

The reverse vane impeller is the only one having true back pull-out design, no measuring of critical tolerances in the field, no setting of seals in the field.

Less Costly Parts Replacement

Erosion/corrosion wear is moved from the expensive casing to the less costly rear cover, thus saving money in parts replacement.

Lower NPSHR Than Front Vane Open Style Impellers

Rear Cover Replacement or Repair vs. Casing Replacement

- The reverse vane design directs abrasive wear between the rear cover and the impeller
- The front open design directs wear between the casing and the impeller
- Casing replacement is two to three times as expensive as the rear cover
- Cover design lends itself to repair by machining or welding
- Weld recovery is 25%-50% of a new cover
- Covers by design have a 1/8 in (3.2 mm) corrosion/wear allowance so damage can be removed by machining. Depending on the alloy or application, welding usually needs to be limited to minor repairs.

Figure 11 – Case Study of Cost Savings Due to RV Impeller Design in One Year

Qty of covers replaced:
5X U.S. $2,500 (Average cost of replacement) = U.S. $12,500

Qty of covers recovered:
6X U.S. $1,000 (Average cost of recovery) = U.S. $6,000

Total: 11   U.S. $18,500

VS.
Casing Maintenance

Qty of casings replaced:
11 X U.S. $5,000 (Average cost of replacement) = U.S. $55,000

Cost savings for RV impeller design per year = U.S. $36,500

CD4MCuN

This duplex stainless steel was co-invented by Flowserve and The Ohio State University. Its hardness is approximately three times greater than that of stainless steel. Its intergranular corrosion resistance is unmatched by any other duplex stainless or 316 stainless steel.

SealSentry™ FML Seal Chamber

The self-venting, self-flushing, self-draining FML seal chamber permits single mechanical seals to be used in more applications. Its solids-handling capabilities are excellent. Initial capital equipment costs are less; evaporation costs due to barrier fluid contamination are considerably less during plant operation. The FML's flow modifiers extend mechanical seal MTBPM.

- Flow modifiers redirect flow from circumferential to axial.
- Balanced flow with low-pressure drop in the chamber helps keep solids in suspension minimizing erosive characteristics of the process.
- A mechanical seal creates a centrifuging action away from its parts and into the returning flow path of the process liquid.
- Solids and slurry merge in the returning flow path and are flushed out of the seal chamber.

ANSI 3 Power End

During the fermentation process it is common to overflow tanks into the ground. It is also common practice to hose down floors and pumps. The ANSI 3 Power End is well suited for this because Inpro® Isolators give protection from hose down and only allow the bearing housing to breathe out. Thus, the oil is kept clean, extending the MTBR of the pumps.

The front end of the ethanol process involves preparing the raw material for fermentation. Generally the corn water mixture is steeped at temperatures up to 185°F (85°C) and a pH of about 2-4. Approximately 20-30% of the ANSI pumps are pumping between 5-35% solids with low pH. The only ANSI pumps in the plant that do not have low pH or solids are the final ethanol pumps.

Caustics are utilized throughout to "Clean In Place" process equipment, thereby making the use of EPR or Aflas O-rings imperative. For final ethanol, the O-rings must be Aflas material because we have seen problems with both Viton and EPR in this application.

Other ANSI 3 Power End benefits include:

- Three-year MTBPM guarantee
- Low shaft deflection index to maximize seal and bearing life
- Lower index of deflection

Baseplates

The standard baseplate for Mark 3 pumps in ethanol production is the Type A standard ANSI baseplate. It is typically foundation mounted but can be used in limited stress stilt mounted configuration. It is the least expensive baseplate offering and, thus, the preferred choice.

There are reinforced baseplate options, but they are more expensive and should be specified selectively when service conditions require it. These include:

- Type B solid polymer concrete for corrosive applications
- Type C for stilt mounted requirements
- Type D flat rigid base for grouting (foundation mounted)

Spare Parts Analysis

Availability of the proper spare parts is imperative to operational availability. Therefore, it is necessary to provide an analysis of all the process pump parts that are used in a plant. This analysis includes the following:

- **Power Frames:** The ANSI pumps will include three different "groups" of power frames – Group 1K, 2K and 3K. Within these groups there is potential to have different shaft materials. In general, the power frames will have 2205 shafts. Stocking suggestion: Three power frame types to the plant's inventory and will repair and reconsign to inventory when necessary.
- **Adapters:** There are up to seven different size adapters. Stocking suggestion: These are not wear items and should not require backup inventory.
- **Mechanical Seals:** In general, there will be three to four different size seals that could be either single or double seals (i.e., six to eight different unique types). Stocking suggestion: Mechanical seals can be the most prone to failure. Therefore, each type of seal should be purchased to a plant's inventory.
- **Impellers:** A plant could use up to 20 different impeller part numbers that include a multitude of impeller trims for each part number. Stocking suggestion: In general, impellers don't fail catastrophically and the factory can ship a trimmed and balanced impeller in 24-48 hours.
- **Covers:** There are up to seven different size rear covers which may have been supplied originally with different materials for each size. Stocking suggestion: Stock each size cover in CD4MCuN material only.
- **Casings:** Due to the RV impeller design and its history with ethanol plants, casings are not a wear item and do not need to be stocked.

Figure 12 – Deflection Comparison

Group 2	Overhang Length	Solid Shaft Diameter	Deflection Index	Shaft w/ Sleeve	Deflection Index
Flowserve	7-11/16 in (189 mm)	1-7/8 in (48 mm)	37	1-1/2 in (38 mm)	90
Major Competitor	8-3/8 in (213 mm)	1-3/4 in (45 mm)	63	1-1/2 in (38 mm)	116

®Inpro is a registered trademark of the Inpro/Seal Corporation.

Training

Training of maintenance personnel will be one of the most important components to the reliability and availability equation. Therefore, Flowserve will offer the following training to a user's maintenance and operations personnel.

- Basic Hydraulics
  - Pump systems
  - System curves
  - Pump curves
  - NPSH
  - Reliability
- Pump Maintenance
  - Basic design
  - Component purpose
  - Tear down
  - Inspection
  - Reassembly
  - Failure analysis
- Mechanical Seal Maintenance
  - Seal types
  - Seal purpose
  - Failure analysis
  - Installation

In addition to our training programs, Flowserve can also offer extensive maintenance support services.
- Cradle-to-grave equipment management including LifeCycle Advantage™ programs to reduce the total cost of ownership and improve operating efficiency
- Upfront services such as product selection, installation and commissioning
- Field performance testing and monitoring (including high energy pumps > 50 kW [65 hp]) to ensure system and energy efficiency
- On-site repairs, laser alignments, technical services and training
- Off-site maintenance and repair services; product overhauls, re-rates and upgrades
- Customized stocking programs
- ISO-ANSI-API pump power and exchange programs
- General machine shop services including seal lapping
- Materials selection and upgrades including hardening, welding and overlay services
- Mechanical seal overhauls and hydrotesting

Section 2: Biodiesel

Background

There are many reasons driving the worldwide enthusiasm for biodiesel fuel. It is viewed as:

- A means for reducing dependence on imported oil and for extending diesel fuel supplies. This is a major issue for countries that are "net importers" of crude oil and/or fuel supplies.
- A more environmentally friendly (carbon neutral) alternative to petrodiesel.
- An alternative to reduce greenhouse gas (GHG) emissions, including carbon dioxide (CO_2), carbon monoxide (CO), particulate matter (PM) and hydrocarbon (HC) emissions. This is a major driver for the European Union (EU) whose member countries are subject to the Kyoto Protocol and thus required to reduce GHG emissions.
- Able to be used in existing diesel engines with proper care and maintenance.
- Compatible with the existing fuel distribution infrastructure.

In 2006 the EU produced 10 million metric tons of biodiesel – a fivefold increase since 2003. Approximately 80% of EU biodiesel was produced from rapeseed. Existing capacity could nearly double output to 20 million metric tons annually depending upon the costs and availability of oil seed feedstock, cost of crude oil, production economics and other factors.

The U.S. produced about 300 million gallons of biodiesel in 2007. By 2012 this output is expected do grow to 1.0 billion gallons annually. Currently, about 90% of U.S. biodiesel is produced from soybean oil. In the coming decade, it is expected that nearly half of U.S. biodiesel will be produced from animal fat and spent cooking oil and grease.

At the end of 2006 there were approximately 185 biodiesel plants operating worldwide. New plant construction in 2007 alone would more than double the number of biodiesel facilities operating globally.

Biodiesel Defined

Like ethanol, biodiesel is categorized as a "bioenergy fuel." Offering substantially reduced CO and CO_2 emissions, lower particulate matter and essentially zero sulfur oxide and sulfate emissions, biodiesel is a clean-burning diesel replacement or renewable fuel that can be used in compression ignition (i.e., diesel) engines. Biodiesel is processed from renewable, nonpetroleum-based sources, including:

- Virgin vegetable oils such as soy, mustard, canola, rapeseed and palm oils
- Animal fats such as poultry offal, tallow and fish oils
- Spent cooking oils and trap grease from restaurants

Biodesiel is produced in pure form (100% biodiesel or B100), but it is usually blended with petrodiesel at low levels, between 2% (B2) to 20% (B20). Blends of biodiesel higher than B5 require special handling and fuel management as well as relatively minor vehicle equipment modifications.

Technically, biodiesel is a methyl ester of a fatty acid (aka FAME). It is most commonly produced by reacting lipids (triglycerides) with a primary alcohol (methanol) and an alkaline base catalyst (sodium hydroxide). This process is referred to as the Base Catalyzation Process. The production reaction, known as transesterification[1], results in the volumetric 10:1 production of biodiesel and glycerine.

When high levels of free fatty acids (> 1.0%) are present in the feedstock, then the Acid Catalyzation Process utilizing sulfuric acid as the catalyst is recommended.

- Caustic
  – Triglyceride + Methanol $\rightarrow$ Methyl Ester + Glycerine

The most common source of triglycerides used for biodiesel production is plant oils and animal fats. Commonly used lipid feedstocks are soybeans (U.S.), canola, sunflower, cottonseed, poultry and beef fats, used cooking oil and rapeseed (EU). The plant oil feedstock most commonly used in Asia is palm oil.

It is important to note that the glycerine produced along with the biodiesel during the catalyzation process can be used in its crude or refined form, and it is a key income stream for today's biodiesel industry. High-purity glycerine is used in the manufacture of pharmaceuticals and cosmetics. Lesser grades are used widely as an industrial chemical in the manufacture of antifreeze, dynamite, solvents, sweeteners, inks and lubricants.

Figure 13 – Basic Biodiesel Flow Diagram
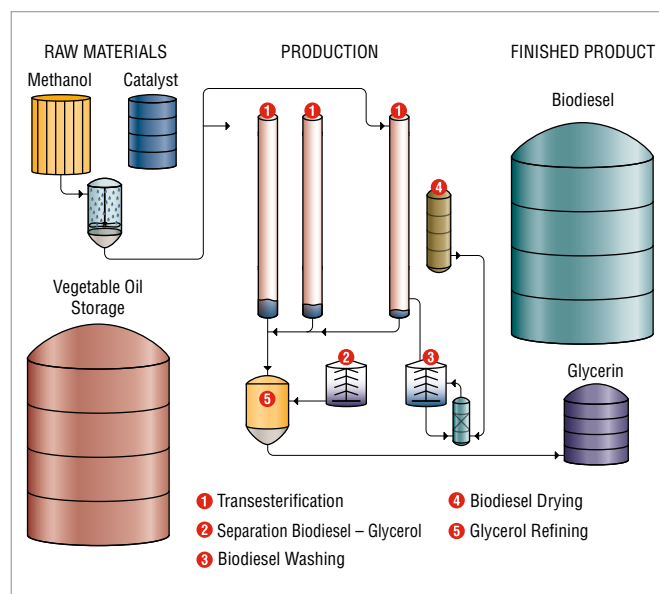
1. Transesterification: the reaction between an ester and another compound with exchange of alleoxyl or acyl groups to form a different ester.

Feedstocks

Although the biodiesel industry has experienced tremendous growth, raw material supplies have served as a natural brake and created a strain on margins for biodiesel producers. The surge in commodities prices is a result of numerous factors including a weak dollar, expanding domestic and global biofuel production capacity, low commodity stocks due to global weather situations, increased energy and transportation costs, and the strength of global food demand. New feedstock opportunities vary significantly because of potential impact on the market in terms of volume and timing to commercialization.

Corn Oil

Ethanol producers may offer the biodiesel industry its nearest term opportunity for additive supplies. Historically, corn oil has not been a viable biodiesel feedstock due to its relatively high cost and high value as edible oil. In current dry grind processes, the corn oil essentially passes through the process and remains in the resulting distillers dry grains with solubles (DDGS). Ethanol firms are investigating fractionating technology to remove corn germ (the portion of the corn kernel that contains oil) prior to the ethanol process.

These technologies could add to the biodiesel raw material supply in a meaningful way. Corn oil could help to meet feedstock market demand in two ways. First is for edible corn oil to displace other edible oils that could then be diverted to biodiesel production. Second is for non-edible corn oil to be used directly for biodiesel production. For example, reaching the proposed goal of 15 billion gallons of ethanol production from corn could generate almost 400 million gallons worth of vegetable oil if only ½ pound of oil was extracted from each bushel of corn.

Soybean Virtual Acres

"Virtual acres" is a term for generating additional feedstock from the same acre. Monsanto plans to introduce new technology that can increase soybean yields 9 to 11%. DuPont is commercializing soybean varieties that increase yields by as much as 12%. These technologies are set to have an impact in 2010. If 90% of U.S. soybean acres adopted the new technology, more than 60 million acres could benefit from a 10% increase in yield. This equates to more than 250 million additional bushels of soybeans (the equivalent of 380 million gallons of biodiesel) without increasing acreage in the U.S.

The same benefit can be achieved by increasing soybean oil content. Current industry genetic programs suggest 10% oil increases are achievable within the next few years.

Camelina and Winter Canola

The production of oilseeds on new acres may also offer additional raw material supplies to the biodiesel industry. Although interest in these oilseeds is high, global wheat consumption has surpassed production in six of the last eight years. The resulting price spike in wheat has negatively impacted the current opportunity for expansion of winter canola and camelina acres.

Camelina

According to Montana State University, camelina is a short season crop (85 to 100 days) that is well suited for marginal soils and has a lower break-even cost than wheat or canola.

Researchers and producers indicate the crop will produce a high quality biodiesel. Typical varieties of camelina are approximately 38 to 40% oil. Depending upon the type of extraction technology used, more than 100 million gallons of oil could be added to the market.

Canola

Canola (rapeseed) is a popular crop throughout the world because of its variety of uses and the nutritional value compared to competing crops. Canola can be produced in some countries where similar crops are not able to grow because of short growing seasons. Although canola oil would primarily move into edible markets, increased acreage will have positive impacts on the overall vegetable oil supply.

Algae

Lipid production from algae holds much promise for the biodiesel industry. Microalgae are microscopic aquatic plants that carry out the same process and mechanism of photosynthesis as higher plants in converting sunlight, water and carbon dioxide into biomass, lipids and oxygen. However, algae production does not require fresh water or arable land used for cultivation of food crops.

Large scale production of these algal lipids is still a few years away but many companies and universities are working to unlock the potential of these single-celled plants, which can contain up to 50% oil by weight and double their numbers in a single day. Once realized oil yield per acre is expected to be the highest of any triglyceride source currently available. Yield projections in the medium term are estimated to range from 2000-5000 gallons per acre as compared to 61 gallons per acre for soybeans.

There are two algae production paths that are being pursued: open ponds or bioreactors. The open pond method involves growing the algae in open ponds of water, much like it grows in nature. Open ponds are generally less capital intensive than the other production methods, but they require a reliable supply of water to replenish that lost from evaporation. The lack of temperature, weather and algae species control can decrease yields from the theoretical potential.

Closed loop or bioreactor systems grow algae in a controlled environment using a wide variety of production processes like plastic

bags, tubes or fermentation reactions. Closed loop systems provide the advantage of additional control over seasonal temperature changes, evaporation losses and contamination by undesired algae strains. However, the capital costs of bioreactors tend to be higher than for open pond systems.

Locating algae processing plants intelligently can add to their efficiency. Locating algae facilities next to carbon producing power plants, or manufacturing plants, for instance, the plants could sequester the CO_2 they create and use those emissions to help grow the algae, which need the CO_2 for photosynthesis.

Very little biodiesel to date has been from algal lipids. Several algae production companies have indicated that the biodiesel has been produced will meet the ASTM D6751 specification. The wide range of algae species will differ in the oils they produce.

Jatropha

Jatropha is a small but versatile bush/tree from the Euphorbiaceae family. The tree flowers and produces clusters of about 10-15 fruits with a seed containing high concentrations of oil. *Jatropha Curcas L.* is gaining a lot of attention as a potential feedstock for biodiesel production due to its high oil content and ability to grow in less than ideal conditions. However, harvesting and logistical challenges have kept the plant from being grown in large scale production in places where there is not an abundance of low cost labor.

Historically, most of the Jatropha has been grown in tropical areas including Africa and Asia, especially India.This low maintenance plant has generally proven to be resistant to local pests under common cultivation practices and can produce seeds containing up to 40 percent oil. While Jatropha is touted as being able to survive in poor soils with very little fertilizer and water, the fruit (and thus oil) yields increase significantly with increased soil fertility and water. For example, adding small amounts of magnesium, sulfur, and calcium have a significant impact on improving yields.

Seashore Mallow

Seashore mallow is a salt-tolerant perennial crop, derived from a salt marsh plant. With an oil content of approximately 18% and residual meal that contains 30% protein, this crop can be grown on saline land and produce vegetable oil on underutilized or non-arable land.

As reported by researchers at the University of Delaware, seashore mallow has a productive life of about a decade and the oil is very similar in fatty acid composition to the oil from cottonseed. Due to limited breeding efforts, yields of seashore mallow are low compared to other oilseeds.

Researchers envision at least four ways that seashore mallow may fit into agronomic scenarios:

- Grown on salinized farmland
- Grown on dry farmland with brackish water wells
- Grown on sandy coastal deserts
- Grown on farmland or aquatic ecosystems in transition

Peanuts

Today, seven states account for approximately 99% of all peanuts grown in the U.S. Georgia grows the major proportion of all peanuts followed by Texas, Alabama, North Carolina, Florida, Virginia and Oklahoma.

Georganic – or similar varieties – may be the future of peanut biodiesel because it can be planted and grown with just one herbicide application for weed control, compared to the three to four applications typically sprayed during a growing season for edible peanuts. Additionally, these fuel peanuts are grown without fungicides, which are the greatest input cost in traditional peanut production.

Currently, there are 24 peanut varieties being scrutinized in this biodiesel screening project, including Georganic, which was developed by ARS breeders in Tifton, Georgia. Promising varieties also include DP-1 and Georgia-04S, a new high-oleic-acid, Spanish-type peanut (ars.usda.gov).

Production of these peanuts would be limited to the southern regions of the U.S. where growing conditions are more suitable.

Chinese Tallow Tree

The Chinese Tallow Tree (*T. sebifera*) is a plant native to central China. The tree is most favorably grown in warm climates with well-drained soils, with the fruit being harvested in early winter after the leaves have fallen off.

According to studies done on the plant properties of the Chinese Tallow Tree, one seed contains about 20% oil, 24% tallow, 11% extracted meat, 8% fibrous coat and 37% shell. The oil keeps well and probably does not need refining. In plantations, when trees are planted about 400 trees per hectare and if pruned would yield 14 MT seed/ha, containing 2.6 MT oil. Some reports yield of 4000 to 10 000 kg/ha, and cite estimates of 25 barrels of oil per year as a sustained energy yield.

The Chinese Tallow Tree is very hard to control, making it seem as if there are no impediments to its growth. It can become invasive. With some tolerance to salt, the Tallow Trees could be investigated as energy crops for saline situations.

Biodiesel Process Explained

Base-catalyzed Transesterification

Transesterification is the most common method used to convert triglycerides to biodiesel. In this reaction, triglycerides react with a short chain alcohol in the presence of a catalyst to produce biodiesel (mono-alkyl esters) and glycerine. Transesterification reactions can be either base-catalyzed or acid-catalyzed, but base-catalyzed is often preferred because it is more rapid than acid-catalyzed. Base-catalyzed is also viewed as being economically advantageous over acid-catalyzed for the following reasons:

- Low temperatures – 60-65°C (140-149°F) – and pressure – 1.4 bar (20 psi) – for processing
- High product yields (> 90%) with lower reaction times
- Direct conversion to alkyl ester with no intermediate steps
- No need for unusual or expensive materials of construction

1. Hawley's Condensed Chemical Dictionary defines transesterification as an ester interchange; reaction between an ester and another compound with exchange of alkoxy or acyl groups to form a different ester.

In base-catalyzed transesterification, alkaline catalysts such as sodium hydroxide (NaOH) and sodium methoxide (NaOCH$_3$) are used. The optimum conditions for forming alkyl esters have been found to be the following:

- The refined oil feedstock should have a free fatty acid content of < 0.5%
- The short chain alcohol should be moisture-free
- Optimum conversion is achieved when the molar ratio of alcohol to oil is 6:1
- The catalysts should be 1.0 NaOH, because it is less expensive
- The catalyst should be stored under anhydrous conditions that are free from air to prevent oxidation of the catalyst

If the above conditions are used, ester conversions of 96-98% are obtained by transesterification of the feedstocks with alcohols like methanol, ethanol and butanol at 60°C (140°F), 75°C (167°F) and 114°C (237°F), respectively, for one hour. Even at 32°C (90°F), vegetable oil can be transesterified in about four hours with an alkaline catalyst.

Figure 14 illustrates a typical base-catalyzed transesterification process flow. The first step in the process is the batch addition of alcohol, vegetable oil and alkaline catalyst into a well-mixed reactor. The reactor is usually heated to just below the boiling point of the alcohol used for the transesterification.

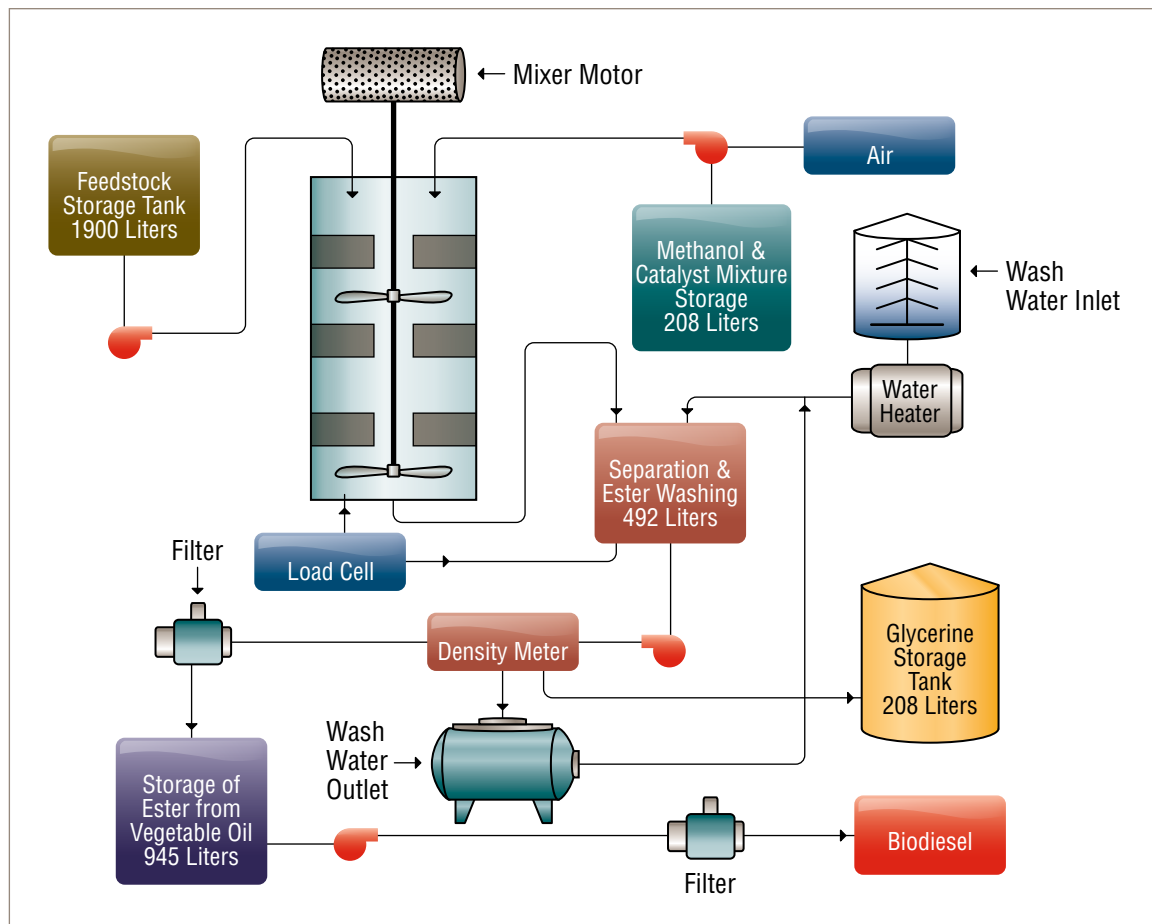*Figure 14 – Base-Catalyzed Transesterification PFD*
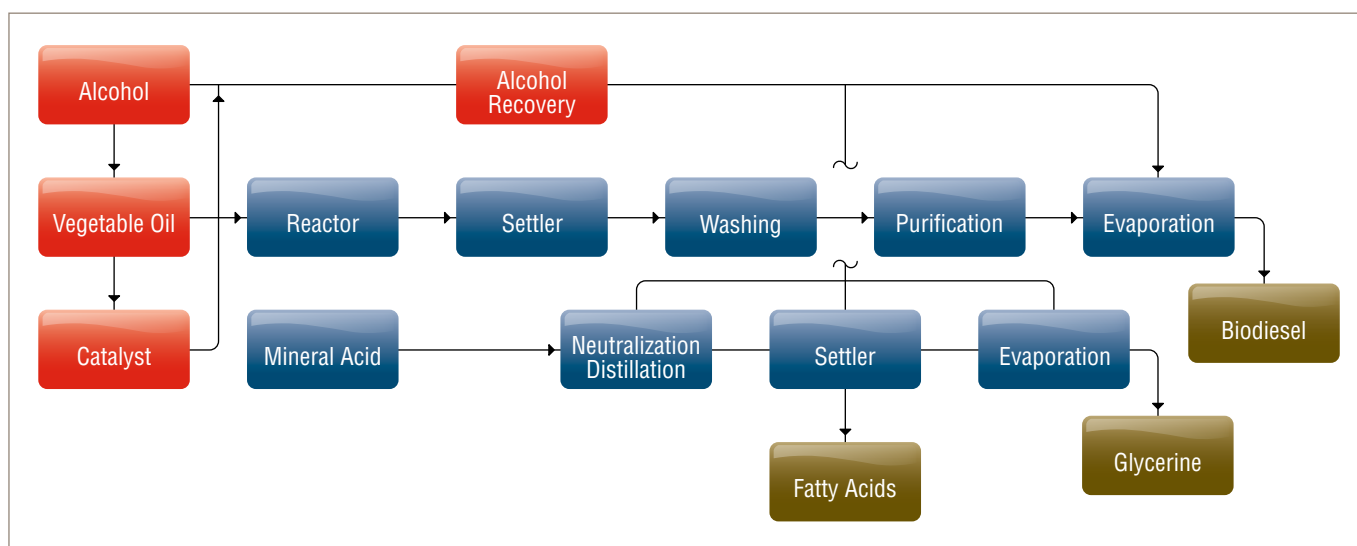
Once the reaction is complete, the products are allowed to separate. The biodiesel layer will settle on top of the glycerine layer. In both layers impurities still exist so more purification steps are usually required. The level of purification depends upon the feedstock source since highly refined oils will have fewer impurities than waste oils or fats. In the case of biodiesel it can be mixed slowly with water using several methods of bubble (preferred method) or mist washing.

Once washing is complete, biodiesel is heated to the point that any remaining water and alcohol will evaporate out of the mixture, leaving pure biodiesel behind. To reduce raw material costs, the alcohol can be recycled back to the alcohol feed stream.

If any free fatty acids are present, they will usually end up in the glycerine layer along with some unreacted methanol. Depending upon the amount of free fatty acids and soap (water-catalyst reaction forms soap) present, the glycerine may need to be purified. If the level of soap is high, the pH of the biodiesel and glycerine will be reduced by adding tannic or acetic acid. After adding mineral acid to the glycerine layer, a sequence of distillation, settling and evaporation can be used to separate the glycerine from the fatty acids and the methanol.

Figure 15 – Base-Catalyzed Transesterification PFD
Source: Canakei and Van Gerpen, 2003

Acid-Catalyzed Transesterification

When the free fatty acid content of the feedstock is > 1.0%, the base-catalyzed reaction does not work very well. Therefore, other methods of transesterification must be used, specifically acid catalysis. Acid-catalyzed transesterification occurs the same way as base catalysis except that an acid catalyst, such as sulfuric acid, is used instead of an alkaline catalyst.

The major difficulty with acid catalysis is that it is slow to convert triglycerides into alkyl esters, although acid catalysts have been found to be effective in converting free fatty acids into esters.

This has led to the design of a process that uses multiple reaction steps: an acid-catalyzed pretreatment step followed by a base-catalyzed transesterification step. (See Figure 16.) The basic idea behind the two-step process is that by reducing free fatty acids to a low level (< 1.0%) by acid catalysis, the quicker base catalysis could be used to actually convert the triglycerides to biodiesel.

With acid catalysis, methanol is most often mixed with the refined vegetable oil. The products of the reaction are methyl esters, glycerine, water, unreacted sulfuric acid and triglycerides that may have been in the feed.

Figure 16 – Acid-Catalyzed Pretreatment Unit With Main Reactor Unit
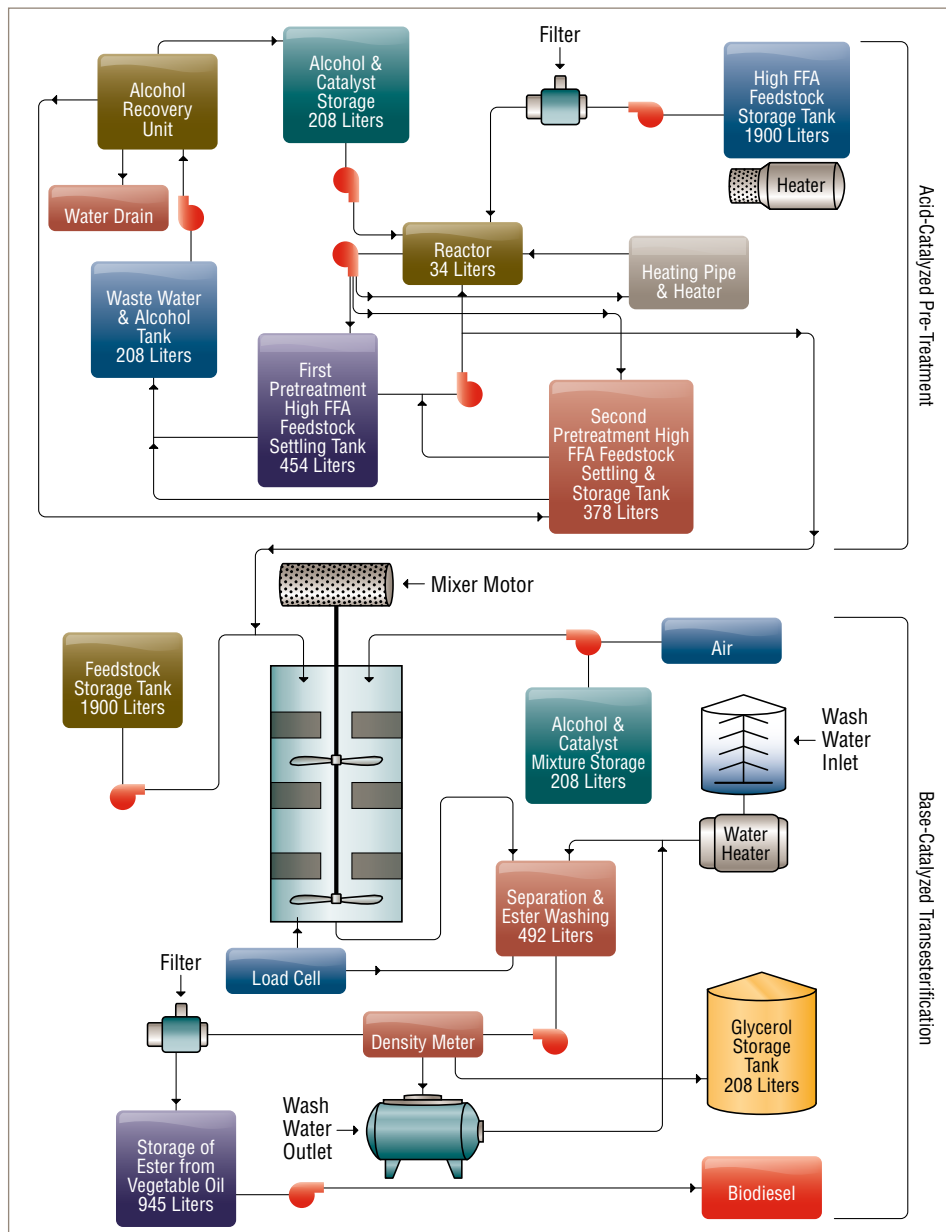*Source: Canakei and Van Gerpen, 2003*

Figure 17 – Pump Types Used to Produce Biodiesel
Source: DeSmet Ballestra

Process Area	No. of Pumps	Type	Casing Materials	Other Comments
Alkali Refining	6	Mixture of positive displacement (alkali dosing) and centrifugal	Mostly SS 304/316 (cast iron for alkali)	Power typically below 10 kW
Transesterification	8	Centrifugal (single-stage horizontal). Mag drive use for methanol addition (by European EPC)	SS 304/316	
Methyl Ester Purification	7	Centrifugal (single-stage horizontal)	SS 316	
Methanol Recovery	7	Mostly centrifugal; metering pumps for acid dosing	SS 316	
Glycerine Recovery	8	Centrifugal	SS 316	

Note:
- Depending upon licensor, process, capacity, on-site refining of feedstock oil and/or glycerine by product, etc., in process between 30 and 50 centrifugal pumps used/plant, up to 5-10 positive displacement pumps for metering/dosing applications
- Additional 15-20 pumps for service and related duties, e.g., unloading, cooling water, effluent, firefighting – bulk and centrifugal
- Total liquid pump purchases per plant (service and process) up to U.S. $1 million to $5 million (up to 200 000 tonnes/year plant)

Miscellaneous Notes

1. Biodiesel is covered under the standard ASTM D 6715-02. This standard defines biodiesel as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. Biodiesel is registered with the U.S. Environmental Protection Agency as a fuel and as a fuel additive under Section 211 (b) of the Clean Air Act (2003).

The policy framework for the development of a biofuels market in the EU is Directive 2003/30/EC. The specification for biodiesel fuel for the EU may be found in EN14214.

2. Animal fat is an attractive feedstock for producing biodiesel. In January 2007, the cost of soybean oil was 33 cents a pound versus 19 cents a pound for chicken fat. It can be processed at the refinery using many of the same chemical processes and much of the existing equipment including pipelines.

In the U.S., Tyson produces about 2.3 billion pounds of chicken fat annually from its poultry plants. That is about 300 million gallons of fat that could be converted into fuel. Tyson has signed an agreement with Conoco Phillips (April 2007) to refine beef, pork and chicken fat into biodiesel. By the end of 2008 a total of about 175 million gallons of renewable diesel annually may be produced across several Conoco refineries.

Turning animal fat into motor fuel is costlier than making conventional diesel. However, U.S. subsidies of $1 dollar-a-gallon biodiesel tax credit narrows that gap while enabling the nation to meet EPACT renewable fuels goals.

Section 3: Cellulosic Ethanol

Background

Cellulosic ethanol is the holy grail of renewable fuels. There are at least five advantages to using cellulosic biomass as the raw materials for biofuels.

- Use of non-food crops. Cellulosic ethanol can be made from just about any kind of agricultural or wood waste material. While ethanol is made from corn kernel, cellulosic ethanol is obtained by processing corn stover (i.e., the leaves and cob). Other feedstock sources include: agricultural residues and wastes (e.g., rice and wheat straw, sugarcane bagasse, fruit pulp and peels); forestry wastes (e.g., hardwood and softwood trimmings); wood wastes (e.g., saw mill and pulp mill waste); and selective municipal wastes. Converting this "trash" into cellulosic ethanol has no direct impact on food and livestock feed prices. In fact, it might even reduce them by providing a market for agricultural waste products.
- Relatively low feedstock cost.
- Use of marginal lands for feedstock growth. An excellent source of cellulosic ethanol is perennial prairie grasses like switchgrass which grow abundantly on marginally fertile ground while providing erosion control and wildlife habitat.
- Beneficial net energy balance. Cellulosic ethanol provides 80% more energy than is required for its production. Cellulosic ethanol reduces greenhouse-gas emissions from 80% below gasoline to completely CO_2 neutral.
- Reduces fertilizer and water usage associated with corn crops.

So, with all its social and environmental benefits, why are we not awash in cellulosic ethanol and OPEC out of business? Two simple reasons:
   – Technology and cost.

Along with cellulose and hemicellulose, cellulosic ethanol feedstocks all contain a substance called lignin. Lignin binds the cellulose molecules together, giving plants the structural strength to stand up and absorb the sun's energy. The gluey lignin also makes plant matter hard to break down. To unlock the cellulose molecules from the lignin, the feedstock is often pretreated with heat and acid. Then it is mixed with high-tech enzymes to break down the cellulose into sugars which can then be fermented into alcohol. The current process turns just 45% of the energy content in the biomass into alcohol, compared with an oil refinery, which extracts 85% of the energy in crude oil. The bio-technology and process technology are still emerging. Most researchers in biofuels expect it will be 10 years before commercial scale production can be achieved.

The second obstacle is cost. Production costs are the main drag on cellulosic ethanol today. DOE estimates that it costs about $2.20 per gallon to produce cellulosic ethanol, twice the cost of ethanol from corn (not including subsidies). Cellulosic plants yield less ethanol than corn per ton of feedstock, and enzymes that break down cellulosic plant tissue costs 30 to 50 cents per gallon of ethanol compared to 3 cents per gallon of corn. To commercialize the industry, production methods and materials need to become better, faster and cheaper.

If the U.S. is to achieve its goal of blending 36 billion gallons of renewable fuels into the nation's gasoline supply by 2022, cellulosic ethanol will have to be the dominant source. There simply is not enough land to grow the corn and soybeans required to produce that much biofuels.

Despite years of ongoing research in the field only a handful of companies are producing cellulosic ethanol on a pilot scale. And none yet is operating on a large commercial level because it is still too expensive to make. Volatile oil prices and significant government support, however, are likely to give cellulosic ethanol a boost to speed up commercialization.

Flowserve is collaborating with Verenium Corporation on a 1.4 million gallon-per-year demonstration-scale facility in Jennings, Louisiana. The facility is designed to process sugarcane bagasse (waste) and specially-bred energy cane into cellulosic ethanol.

Other players in the cellulosic ethanol market include:

- Iogen Corporation, a Canadian biotechnology firm, became the first business to commercially sell cellulosic ethanol in 2004.
- Abengoa Bioenergy (Spain) is building a 5 million gallon-per-year facility using process and pre-treatment technology from Sun Opta Inc. (Canada).
- GreenField Ethanol, Canada's largest ethanol producer, entered a joint venture with Sun Opta to build a series of large-scale plants to make cellulosic ethanol from wood chips.
- Range Fuels (U.S.) in July 2007 obtained a permit from Georgia to build the first commercial-scale 10 million gallon-per-year cellulosic ethanol plant.
- DuPont is working with DOE to make cellulosic ethanol out of corn stover.
- Chevron is working with DOE and the University of California at Davis on joint cellulosic ethanol fuel ventures.
- In January 2008 General Motors announced it has taken a stake in Coskata, Inc. (Warrenville, Illinois) to produce cellulosic ethanol on a commercial scale.

Cellulosic Ethanol Defined

Cellulosic ethanol (CE) is chemically identical to conventional ethanol derived from grain. Hawley's Condensed Chemical Dictionary defines ethanol as follows:

Ethyl Alcohol

(alcohol; grain alcohol; ethanol; EtOH).
CAS: 64-017-5, C2H5OH.

Properties

(Pure 100% absolute alcohol, dehydrated) Colorless, limpid, volatile liquid; ethereal vinous odor; pungent taste. Bp 78.3°C, fp – 117.3°C, refr index 1.3651 (15°C), surface tension 22.3 dynes/cm (20°C), viscosity 0.0141 cP (20°C), vap press 43 mm Hg (20°C), specific heat 0.618 cal/g K (23°C), flash p 55°F (12.7°C), d 0.816 (15.56°C), bp 78°C, fp–114°C, autoign temp 793°F (422°C). Miscible with water, methanol, ether, chloroform and acetone. (95% alcohol)

CE is derived from biomass, a term encompassing everything from waste materials like corn stover and paper pulp to fast-growing perennial plants like switchgrass, willow and poplar. Cellulosic biomass is composed of cellulose (40-50%), hemicellulose (20-30%) and lignin with smaller amounts of proteins, lipids (fats, waxes and oils) and ash. Roughly two-thirds of this cellulosic matter is complex carbohydrate, which can be broken down into fermentable sugars and then fermented into alcohol. Add a splash of gasoline and it becomes ethanol. Like conventional ethanol, a gallon of CE yields about two-thirds the energy of a gallon of gasoline.

Lignin, a waste by-product, has an energy content similar to that of coal. In most CE production models, the lignin is recovered and burned to power the process, thus closing the energy loop.

The economics of CE versus grain-based ethanol clearly favor CE.

• Feedstock is cheap and abundant.
• An acre of grasses or other crops grown specifically to make ethanol could produce more than two-times the number of gallons of ethanol as an acre of corn.
• Less fossil fuel is required to process it.
• It emits 80% less global warming pollution than gasoline.

With all of these advantages, however, CE is still not commercially feasible as process and production costs remain significantly higher than conventional ethanol. Reducing the cost and improving the efficiency of separating and converting cellulosic materials into fermentable sugars is essential to making CE viable. Government and private R & D efforts are focusing on the development of cost-effective biochemical hydrolysis and pretreatment processes. The race to find a new generation of super cellulose-busting enzymes is on.

Cellulosic Ethanol Process Explained

There are two ways of producing alcohol from cellulose:

• **Cellulolysis** (i.e., biological) processes which consist of hydrolysis on pretreated lignocellulosic materials to break down the complex carbohydrates into simple sugars, followed by microbial fermentation yielding ethanol and CO_2.
• **Gasification** (i.e., thermochemical) processes that transform the lignocellulosic materials into synthesis gases (CO_2, carbon monoxide and hydrogen) and then converts them to ethanol by microbial fermentation or chemical catalysis.

Of these two approaches, cellulolysis (cellulose hydrolysis) is by far the most prevalent and the one which will be explained in detail.

Cellulolytic Processes

The object of processing cellulosic biomass is to extract fermentable sugars from the feedstock. But the sugars in cellulose and hemicellulose are locked in complex carbohydrates called polysaccharides (long chains of monosaccharides or simple sugars). Separating these complex polymeric structures into fermentable sugars is essential to the efficiency and economics of CE.

Two processing options are employed to produce fermentable sugars from cellulosic biomass. One approach utilizes acid hydrolysis to break down the complex carbohydrates into simple sugars. An alternative method, enzymatic hydrolysis, utilizes pretreatment process to first reduce the size of the material. This makes it more accessible to hydrolysis. Once pretreated, enzymes are employed to convert the cellulosic biomass to fermentable sugars. The final step involves microbial fermentation yielding ethanol and CO_2.

It is important to note that the sugar in cellulose is locked up in the form of cellulose and hemicellulose. Cellulose contains glucose, the same type of sugar, a six-carbon (C6) sugar, that is found in cornstarch and that can be fermented to ethanol using conventional yeasts. However, hemicellulose contains mainly non-glucose sugars, five-carbon (C5) sugars, which cannot be fermented to ethanol using conventional yeasts. The keys to commercial-scale production of CE are the development of custom enzymes and yeasts which can maximize fuel output.

Figure 18 – The Process of Making Ethanol From Cellulosic Biomass
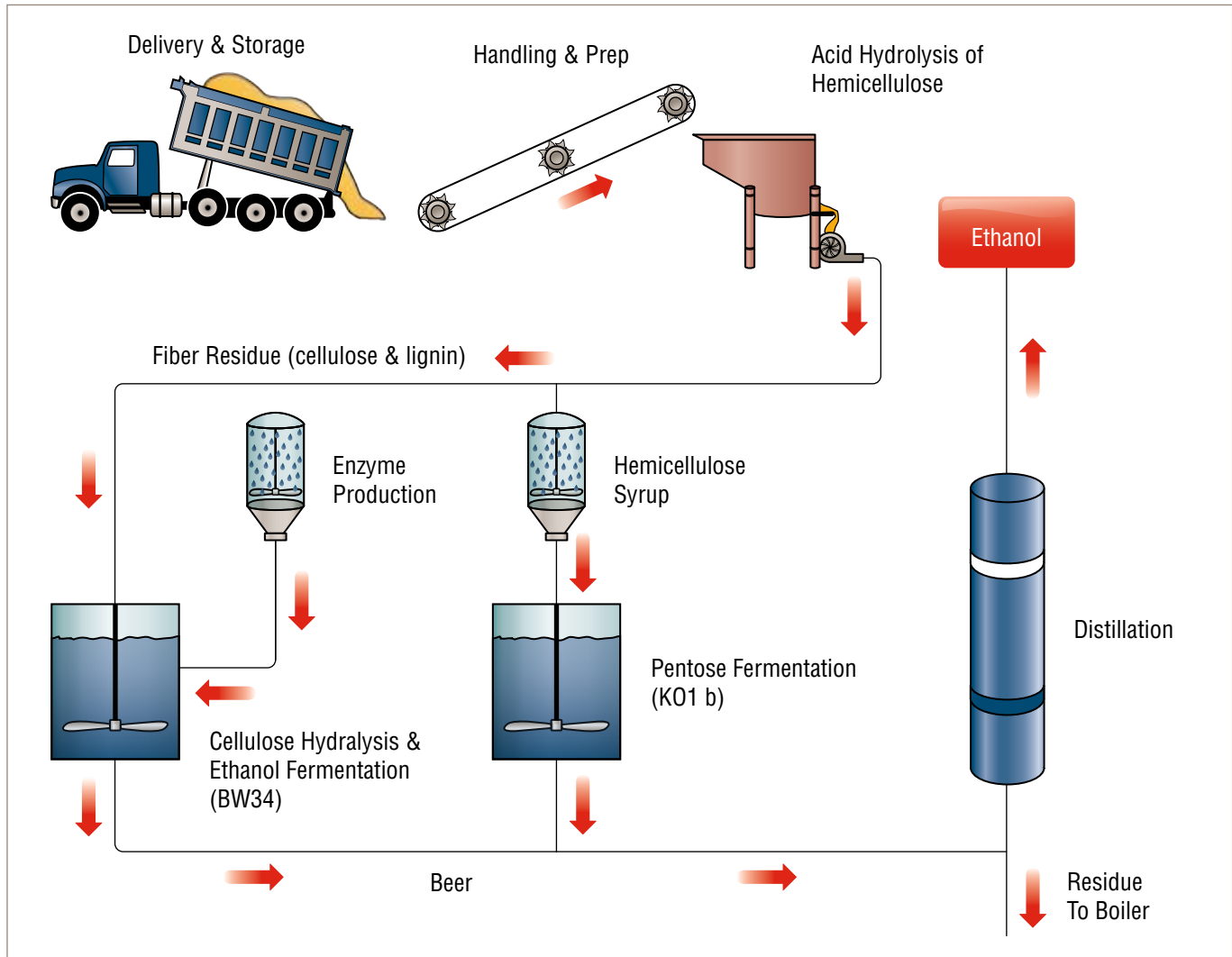
Biomass Handling

Biomass goes through a size-reduction step to make it easier to handle and to make the ethanol production process more efficient. Agricultural waste goes through a grinding process while wood waste is chipped to achieve a uniform particle size.

Biomass Pretreatment

The hemicellulose fraction of the biomass is reduced to simple sugars. A chemical reaction (i.e., hydrolysis) occurs when dilute sulfuric acid is mixed with the biomass feedstock. In this hydrolysis reaction, the complex chain of sugars that make up the hemicellulose sugars are converted to a mix of soluble 5C sugars (i.e., xylose and arabinose) and soluble 6C sugars (i.e., mannose and galactose). A small portion of the cellulose is also converted to glucose.

Other pretreatment techniques include:

• steam explosion
• ammonia fiber expansion (AMFE)
• alkaline wet oxidation
• ozone

Of these, AMFE shows the most promise. This technique employs liquid ammonia under moderate heat and pressure to break the hemicellulose/lignin sheath that surrounds the cellulose in plant material.

Enzyme Production

The cellulase enzymes that are used to hydrolyze the cellulose fraction of the biomass are grown in this step. Alternatively, the enzymes may be purchased from commercial enzyme suppliers.

Cellulose Hydrolysis

The remaining cellulose is hydrolyzed to glucose. In this enzymatic hydrolysis reaction, cellulase enzymes are used to break the chains of sugars that make up the cellulose, releasing glucose. Cellulose hydrolysis is also called cellulose saccharification because it produces sugars.

Glucose Fermentation

The glucose is converted to ethanol through fermentation, a series of chemical reactions that converts sugars to alcohol. The fermentation reaction is caused by yeast or bacteria which feed on the sugars. As the sugars are consumed, alcohol and carbon dioxide are produced.

Pentose Fermentation

The hemicellulose fraction of biomass is rich in C5 sugars, which are also called pentoses. Xylose is the most prevalent pentose released by the hemicellulose hydrolysis reaction. Xylose is fermented by using a genetically engineered bacteria.

Ethanol Recovery

The fermentation product from the glucose and pentose fermentation is called ethanol broth and must be distilled. In this step the ethanol is separated from the other components in the broth. A final dehydration step removes any remaining water to produce 99.5% pure alcohol.

Lignin Utilization

Lignin and other by-products of the biomass-to-ethanol process can be used to produce the electricity necessary for the ethanol production process.

Gasification Process

Background

Gasification was originally developed in the early 1800s. It was used to produce "town gas" (syngas) from coal for lighting and cooking. Town gas was used to light city streets and homes before natural gas and electricity were introduced for that purpose.

By the early 1900s, syngas had fallen out of general public use, replaced by electricity and natural gas. Since the 1920s syngas has been used mostly for the production of synthetic fuels and chemicals, especially during times of war when petroleum-based fuels were at a premium or unavailable. Some nations (notably the Union of South Africa) have used gasification to produce a gasoline substitute for transportation fuels, because domestic petroleum sources were lacking and oil was difficult to import.

Today, concerns about energy security and volatile global fuel costs are causing increasing interest in using gasification as an energy resource.
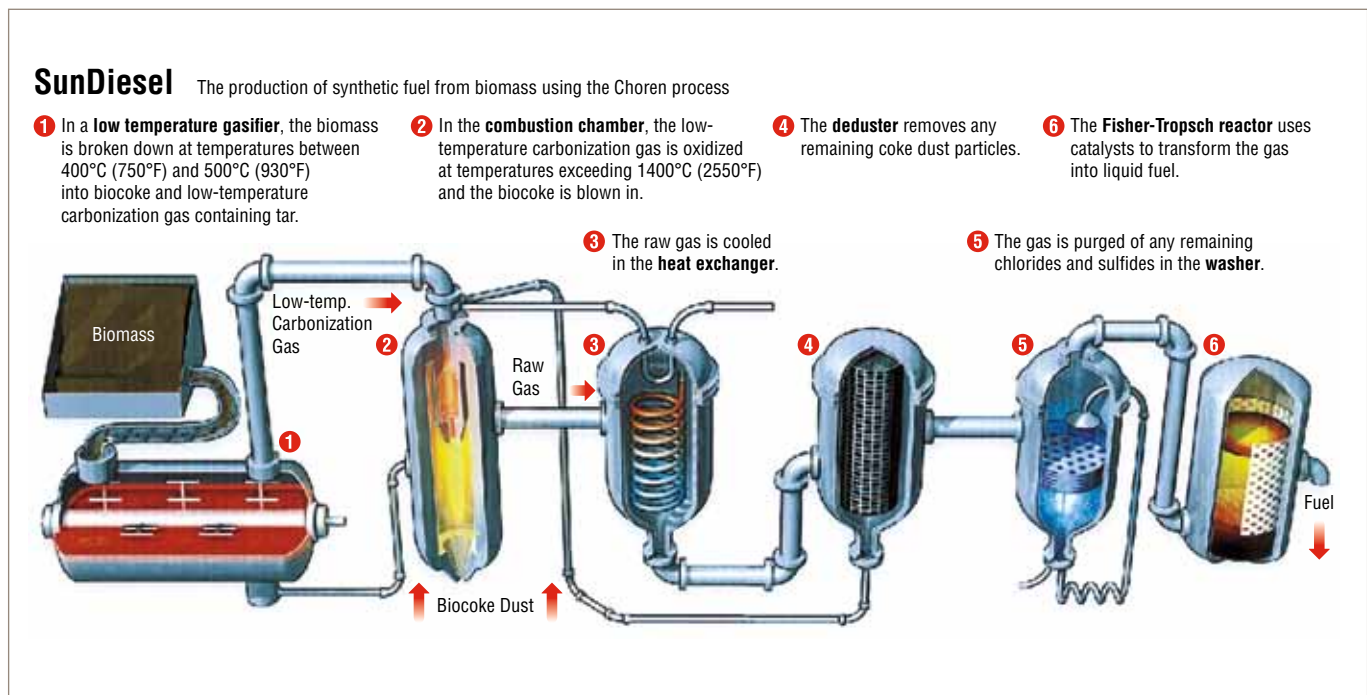
The Gasification Process Explained

Gasification is usually associated with the conversion of coal to liquids (CTL) for transportation fuels and with the conversion of biomass to heat/combined heat and power (CHP) largely for electricity generation. Yet it can also be employed to convert biomass – municipal solid waste, agricultural and wood residues – into diesel fuels (BTL), lubricating oil, chemical feedstock and fertilizer.

As related to biomass conversion, there are two types of gasification:

1. Hybrid thermochemical and biological system. Biomass materials are first thermochemically gasified and the synthesis gas (a mixture of hydrogen and carbon oxides) is bubbled through specially designed fermenters. A microorganism (Clostridium bacteria) that is capable of converting the synthesis gas is introduced into the fermenters under specific process conditions to cause fermentation to ethanol. (See Figure 19.)

Figure 19 – Gasification Process

SunDiesel The production of synthetic fuel from biomass using the Choren process

1. In a **low temperature gasifier**, the biomass is broken down at temperatures between 400°C (750°F) and 500°C (930°F) into biocoke and low-temperature carbonization gas containing tar.

2. In the **combustion chamber**, the low-temperature carbonization gas is oxidized at temperatures exceeding 1400°C (2550°F) and the biocoke is blown in.

3. The raw gas is cooled in the **heat exchanger**.

4. The **deduster** removes any remaining coke dust particles.

5. The gas is purged of any remaining chlorides and sulfides in the **washer**.

6. The **Fisher-Tropsch reactor** uses catalysts to transform the gas into liquid fuel.

Low-temp. Carbonization Gas

Biomass

Raw Gas

Biocoke Dust

Fuel

2. The second all-thermochemical ethanol production process does not use any microorganisms. In this process, biomass materials are first thermochemically gasified and the synthesis gas passed through a reactor containing catalysts, which cause the gas to be converted into ethanol. In effect, diesel fuel is obtained via the Fischer-Tropsch reaction. (See Figure 20.)

External yields up to 50% have been obtained using synthesis gas-to-ethanol processes. Some processes that first produce methanol and then use catalytic shifts to produce ethanol have obtained ethanol yields in the range of 80%. Unfortunately, like all gasification processes, finding a cost-effective all-thermochemical process has proven difficult. This (i.e., the economics) and not the technology has been the barrier to commercial-scale BTL.

Pumping Cellulosic Ethanol

Please refer to Section 1: Ethanol, pp 8 and ff.

How expensive is BTL gasification vis à vis other conversion processes?

According to the EIA's "Annual Energy Outlook 2006," capital costs are:
U.S. $15,000 - $20,000 per installed barrel for a conventional oil refinery; U.S. $20,000 - $30,000 for an ethanol plant; approximately U.S. $40,000 for gas-to-liquids (GTL); approximately U.S. $60,000 for coal-to-liquids (CTL); and U.S. $120,000 - $140,000 for biomass-to-liquids (BTL).

Figure 20 – Process Design Overview
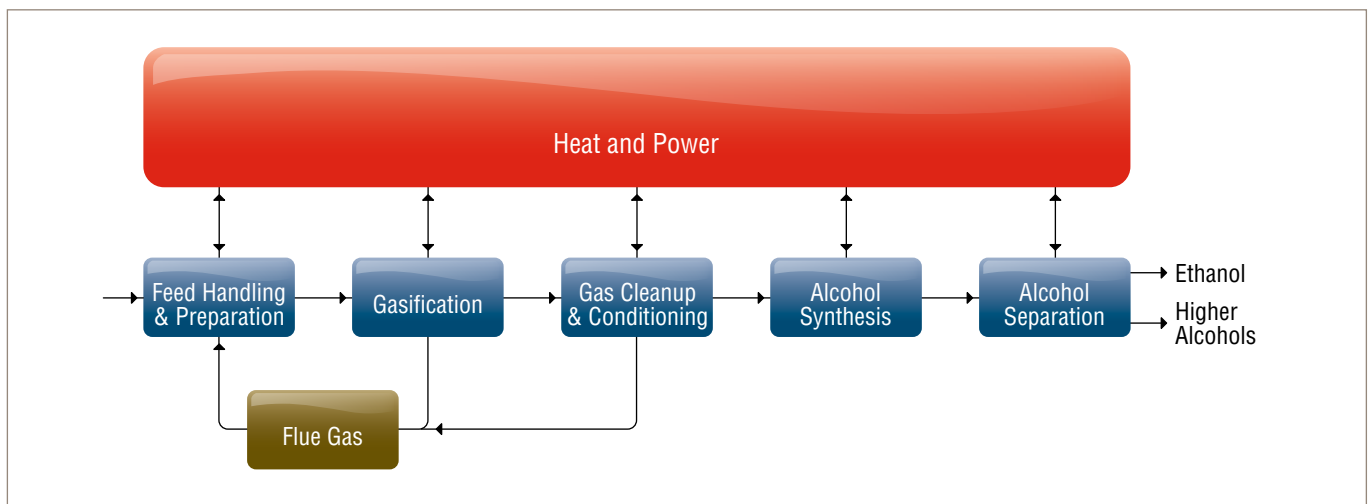
Definitions

- **Fischer-Tropsch Process**
  Synthesis of liquid or gaseous hydrocarbons or their oxygenated derivatives from the carbon monoxide and hydrogen mixture (synthesis gas) obtained by passing steam over hot coal. The synthesis is carried out with metallic catalysts such as iron, cobalt or nickel at high temperature and pressure. The process was developed in Germany in 1923 by F. Fischer and H. Tropsch and was used there for making synthetic fuels before and during World War II. It has never been used for this purpose in the U.S.; the only coal-to-gasoline conversion plant using this process is Sasol in South Africa, though the closely rated Lurgi process is being used rather extensively in a number of locations. Easing of the petroleum crisis has tended to diminish conversion activity in the U.S.

- **Fischer-Tropsch Synthesis**
  (Synthol process; Oxo synthesis). Synthesis of hydrocarbons, aliphatic alcohols, aldehydes, and ketones by the catalytic hydrogenation of carbon monoxide using enriched synthesis gas from passage of steam over heated coke. The ratio of products varies with conditions. The high-pressure Synthol process gives mainly oxygenated products and addition of olefins in the presence of cobalt catalyst (Oxo synthesis) produces aldehydes. Normal-pressure synthesis leads mainly to petroleum-like hydrocarbons.

Section 4: Biobutanol

Background

n-butanol is exhibit one in the old adage: "Everything old is new again." For the first half of the 20th century, the dominant route for making butanol for solvent and chemical applications was the acetone-butanol-ethanol (ABE) bacterial fermentation process. Over the years, improvements have been made to the ABE process to increase yield and to produce different ratios of the three solvents. Various strains of the bacterium *Clostridium acetobutylicum* and different feedstocks, such as corn and molasses, were employed along with nutrients to improve the overall fermentation.

During the 1950s, the ABE process was eclipsed by lower cost and more efficient petrochemical processes, although fermentation continued in the U.S.S.R. into the 1980s and continues in China today.

Today, however, rising oil prices, concerns surrounding climate change and national security have rejuvenated interest, research and development into biobutanol. A large number of major industrial companies and venture-capital financed biotech firms are pursuing microbial technology to commercialize biobutanol production. For example, BP and DuPont have a joint venture to commercialize and market ABE-made biobutanol from China by 2010.

It is becoming increasingly clear that biobutanol can be produced commercially today, unlike other advanced biofuels being proposed, such as cellulosic ethanol, fermentation hydrocarbons and algal biodiesel. Initially, however, biobutanol's value as a chemical product will be much higher than its value as a transportation fuel. With time, biobutanol can be expected to overcome ethanol as the production economics are realized in facilities aimed at chemical markets, as the process is improved to lower costs and as butanol's qualification as a fuel are proven.

To summarize, biobutanol will be a bridge between today's bioethanol and biodiesel fuels and tomorrow's cellulosic derived fuels. Additionally, it will provide high-value chemical product alternatives to petroleum-based ones.

Biobutanol Defined

Butanol is a 4-carbon alcohol (butyl alcohol). The dominant petrochemical process today is the propylene-based oxo synthesis process in which aldehydes from propylene hydroformylation are hydrogenized to yield n-butanol.

Biobutanol can be produced by fermentation of biomass by the ABE process. The process uses the bacterium *Clostridium acetobutylicum*, also known as the Weizmann organism. In 1916 Chaim Weizmann first used this bacteria for the production of acetone from starch. (The acetone was used to make smokeless gunpowder and a propellant for rockets.) The butanol was a by-product of this fermentation. The process also creates a recoverable amount of H_2 and a number of other by-products: acetic, lactic and propionic acids, acetone, isopropanol and ethanol.

While fermentation by bacteria is still the standard, companies such as NovoZymes (USA) and Butalco (Switzerland) are developing genetically modified yeasts for the production of biobutanol from biomass.

The production of bioethanol and biobutanol has many similarities. The feedstocks are the same: energy crops such as sugar beets, sugar cane, corn grain, wheat, etc., as well as agricultural by-products such as straw and corn stalks, bagasse, etc. The difference between the two production processes is primarily in the fermentation of the feedstocks and minor changes in distillation.

Biobutanol fermentation differs from bioethanol fermentation mainly in the use of bacteria rather than yeast, and a less energy-intensive but more complex product separation scheme. According to DuPont, existing bioethanol plants can cost effectively be retrofitted to biobutanol production as little capital is tied up in the distillation unit vis à vis feedstock preparation, fermentation, initial separation, by-product handling and offsites.

Butanol's Uses

- Chemicals
  The acetone-butanol-ethanol can be used in the production of other chemicals, synthetic rubber and plastics (including safety glass), hydraulic fluids and detergents… also in solvents for paints, coatings, varnishes, resins, dyes, vegetable oils and waxes. End-products include textiles, flotation agents, cleaners, floor polishes, antibiotics, vitamins and hormones.

- Biofuels
  Biobutanol offers several advantages over ethanol as a biofuel:
  – Can be easily added to conventional gasoline due to its low vapor pressure
  – Has an energy content closer to that of gasoline, therefore less compromise on fuel economy
  – Can be blended at higher concentrations than bioethanol for use in standard vehicle engines
  – Is less susceptible to separation in the presence of water than ethanol/gasoline blends. Therefore, it is suitable for transport in existing pipelines and distribution in existing infrastructures, i.e., blending facilities, storage tanks, retail station pumps
  – Significantly less GHG and pollutants

Biobutanol Process Explained

Biobutanol is produced from the same agricultural feedstocks as ethanol, i.e., corn, wheat, sugar beet, sugar cane, sorghum, cassava, etc. It can also be produced from agricultural waste or biomass. Existing ethanol capacity can be cost effectively retrofitted to biobutanol capacity with relatively minor changes in fermentation and distillation.

Biobutanol relies heavily upon bacteria fermentation, although some enzyme-catalyst companies are developing yeast as fermentation agents. And while ethanol distillation relies upon multiple distillation columns, biobutanol is likely to utilize a single reaction-fractionation tower similar to existing petrochemical plant equipment. While more complex, the single fractionation unit will utilize less energy to operate and be relatively simple and inexpensive to retrofit.

For a comprehensive description of the ethanol production process, please see Section 1: Ethanol, pg 3 and ff.

A Bridge to Cellulosic Ethanol

Biobutanol has been described as a bridge to cellulosic ethanol because it will use both energy crops and biomass (i.e., agricultural waste) in the production of butanol-based fuels and chemicals.

The production of biobutanol from agricultural residues involves four steps:

• Pretreatment which opens the wall structure and removes lignin
• Hydrolysis of hemicellulose and cellulose into simple hexose and pentose sugars using enzymes
• Fermentation of simple sugars into butanol using bacteria, and
• Recovery of the butanol

There are two issues which must be successfully addressed to make biobutanol commercially viable. The first is to replace the need for expensive enzymes used in lignin destruction with bacteria. The second is to combine the hydrolysis-fermentation-recovery production steps into a single reactor.

Biobutanol can be produced from biomass by either fermentation or thermochemical processes. The challenge for developing biobutanol (as described previously) is improving the technology to the point where it is capable of producing commercial volumes which remain economically competitive, first against oxo synthesis petrochemicals and later versus petroleum-derived fuels.

Currently, there are five conversion methods, four fermentation and one thermochemical, which are under serious consideration and development for commercial biobutanol product.

• Fermentation
  – The classic *Clostridium acetobutylicum* ABE fermentation
  – The current best-in-class BA101 (an anaerobic bacterium) fermentation developed by Hans Blaschek (University of Illinois at Urbana-Champaign) and licensed to Tetravitae Bioscience (www.advancedbiofuelsinc.com). This process involves the continuous fermentation of corn without continuous removal of solvents, and it could easily be adapted to convert corn ethanol mills to biobutanol production.
  – The two-step dual immobilized reactors with continuous recovery (DIRCR) process patented by David Ramey of Environmental Energy, Inc. (www.butanol.com). Using corn as the feedstock, this process first converts corn to butyric acid, then butyric acid to butanol.
  – The condensation of bioethanol to biobutanol, aka Guerbet Catalysis

• Thermochemical
  – Biomass gasification followed by syngas catalysis. See Section 3: Cellulosic Ethanol, pg 25.

Figure 21 – Biobutanol Made By Various Fermentation and Thermochemical Processes
Source: CEP
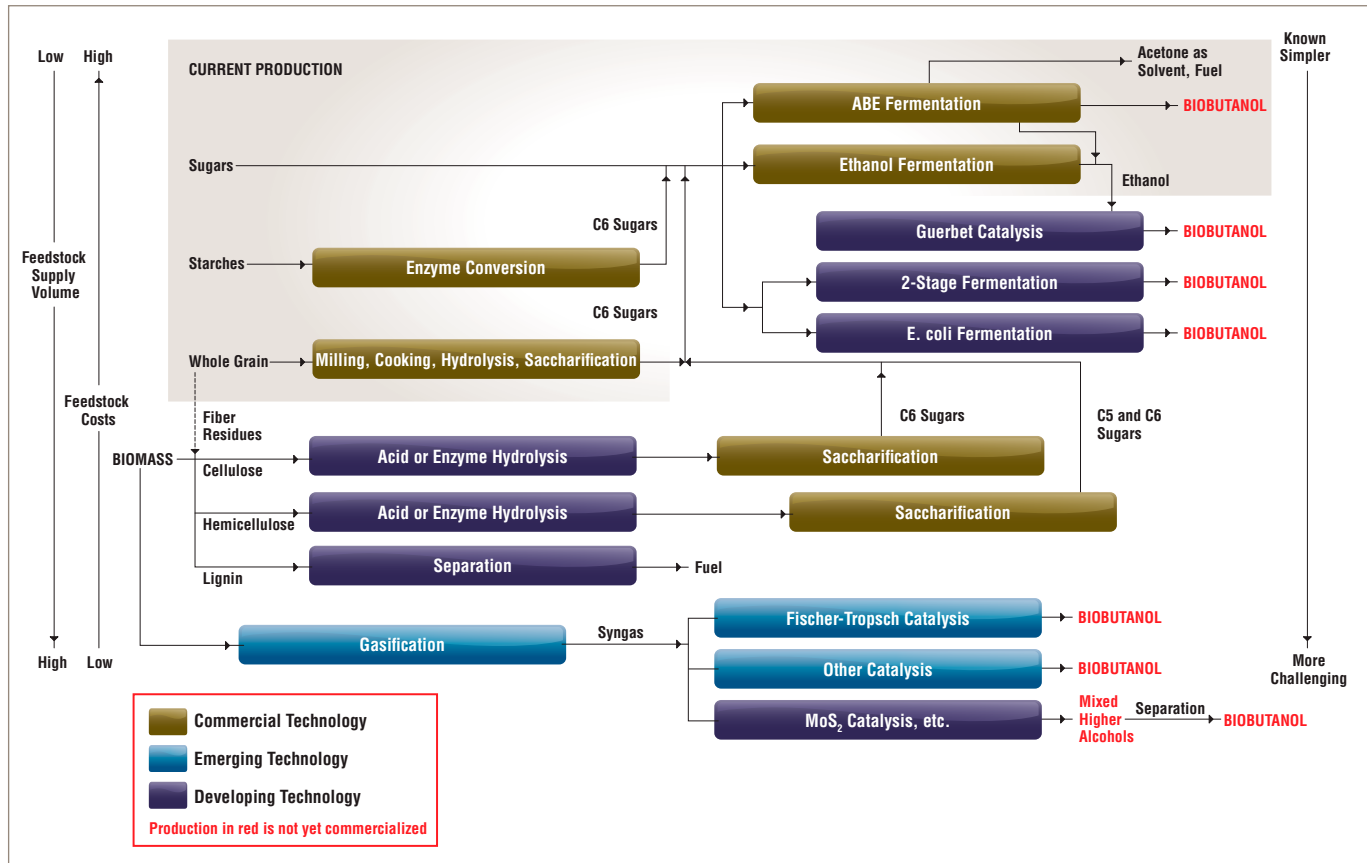
Conclusion:

The production of biobutanol by biological routes is a well-known commercial technology which can be returned to use and further improved. Biobutanol is likely to be more widely commercialized by taking market share from synthetic butanol in the industrial chemical and solvent markets before it obtains a significant market share as a fuel at lower prices.

Biobutanol has several important characteristics that give it key advantages. It can be blended at the oil refinery, relieving pressure on the logistics of ethanol distribution, refueling and use in gasoline engines. Existing ethanol manufacturing facilities can be adapted to produce biobutanol. Cellulose can be more readily used as a feedstock in combined hydrolysis and fermentation processes. Biobutanol can also be produced by the catalytic condensation of ethanol, as well as by biomass gasification. And, it can be blended into both gasoline and diesel fuel.

There is no question the commercialization of biobutanol is at hand as evidenced by the DuPont/BP joint venture to begin production in 2010. But will there be one or several licensed process winners? Will one process become dominant? Will new biobutanol "refineries" be built or will the majority of biobutanol be produced by refitted corn ethanol mills? Many questions but few answers.

Pumping Biobutanol

Biobutanol pump applications are expected to closely mirror those used in ethanol production. For a comprehensive discussion of applications, pump models, pump features and benefits, materials, specification, etc., please see Section 1: Ethanol, pp 8 and ff.

Section 5: Biorefineries

Background

Renewable fuels is only one part of the cellulose conversion story, albeit the most publicized to date. But plant biomass holds significant promise for the production of a diverse range of products, including chemicals, polymers, lubricants, adhesives, fertilizers, animal feed and even energy for power generation.

Downstream Products

Green Chemicals
- Organic commodity chemicals, including solvents, fuel additives, lubricants, surfactants, adhesives and inks
- Fine chemicals, including enzymes, nutraceuticals and pharmaceuticals
- Chemical intermediates, such as sugars, organic acids (e.g, levulinic acid), and monomers or monomer precursors

Renewable Plastics
General categories include plant-based degradable polymers, carbohydrate (cellulose, starch and chitin) polymers and lignin polymers. Examples include starch esters, celluose acetate blends, polylactide (PLA), polyhydroxybutyric acid (PHB) and thermoplastic proteins.

Natural Fibers
In addition to improved pulp and paper processes, new products are being developed based on natural fibers including insulation and geotextiles for soil erosion control.

Bioremediation
Enzymes, microorganisms and plants are the major groups of bioremediation catalysts.

Some corn processors, for example, are converting corn sugar into momomer and lactide acid to form the building blocks of renewable chemicals. Corn, soybeans and other crops are now showing up in take-out food packaging and disposable cups, textiles and carpet, automotive and furniture foam cushions, even AstroTurf. As with biofuels, however, the real future of biochemicals lies within cellulose and the unlocking of its potential.

Biotechnology visionaries foresee biorefineries dotting the plains of the American Midwest, western Canada and Eastern Europe. The concept is very similar to that of a petroleum refinery which converts crude oil into fuels and petrochemical feedstock. Biorefineries exhibit some important differences, however. First, biorefineries can utilize a variety of feedstock and, therefore, will require a broader range of processing technologies to deal with the compositional differences in the feedstock. Second, the biomass is bulkier (i.e., contains a lower energy density) relative to fossil fuels. As a result, economics dictate decentralized biorefineries located close to feedstock sources. Think of a rural site in Nebraska versus the facilities concentration in the Houston shipping channel.

The production of green chemicals, it should be noted, is good for business profits and for the health of the environment. Biochemicals are made from cheap, plentiful biomass and the waste products in the biofuels conversion process. The lignin residue (similar to coke residuum in delayed coking) can be used to provide electricity for the biorefinery. DuPont has found that its Bio-PDO™ (propanediol) consumes 40% less energy to produce and reduces greenhouse gas emissions by 20% versus petroleum-based propanediol. And Bio-PDO is biodegradable.

Biorefinery Processes

Biorefinery process technology is still largely in the conceptual stage, although demonstration-scale plants are being built. The National Renewable Energy Lab's (NREL) biorefinery concept is based upon two different "platforms" to utilize different product slates.

The "sugar platform" is based on biochemical conversion processes and focuses on the fermentation of sugars extracted from biomass feedstocks (i.e., grain and cellulose). The "syngas platform" is based on thermochemical conversion processes and focuses on the gasification of biomass feedstocks and by-products from conversion processes. See Section 3, Cellulosic Ethanol, for a description of these biological-based and thermochemical-based processes.

The term "biorefinery" has been used to describe the envisioned but as yet unrealized paradigm for converting lignocellulosic biomass and other sources of biomass (e.g., municipal solid waste) into valuable products. The biorefinery is analogous to the petroleum refinery: biomass is "cracked" into separated components and each is converted to a distinctly marketed product. A biorefinery, then, is a processing plant that refines biomass (see Figure 4).

Figure 22 – Bioproducts From Low Value Biomass Derived Feedstocks
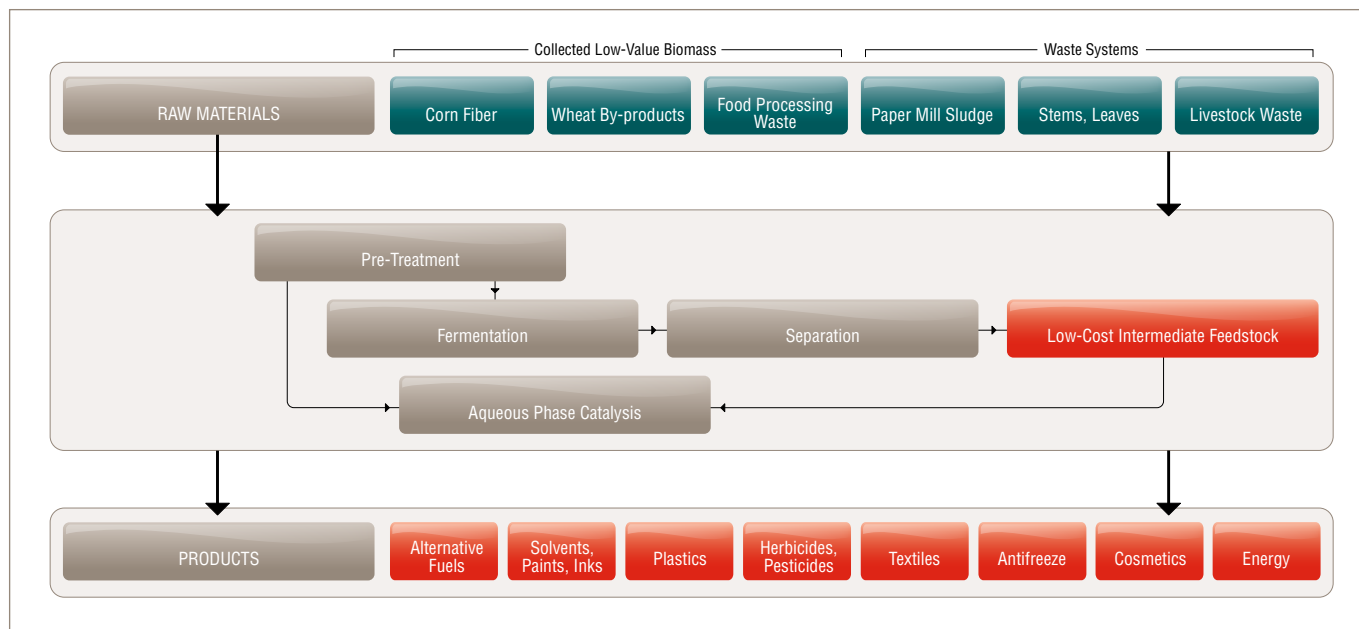
As stated previously, biomass can be converted into fuels and chemicals either biologically or thermochemically. Mechanical conversion is also practical and proven.

Biological conversion of biomass can be accomplished by enzymatically hydrolyzing cellulose and hemicellulose to sugars that are subsequently fermented into products, e.g., alcohols and carboxylic acids.

Thermochemical conversion of biomass involves partial oxidation to produce synthesis gas (i.e., $CO + H_2$), which can be catalytically converted to a variety of products, i.e., alcohols and hydrocarbons. Product yields are comparatively lower, however, because the biomass is partially oxidized.

A summary of the biorefinery processes and products is presented in Figure 22.

Current Activity

The traditional chemical and food processing industries are buying into the biochemical marketplace. DuPont, Cargill, ADM, Purac, Novamont, Roquette, Rodenburg, BASF, P&G, Innovial, et al., have active development and production-scale programs.

Bio-based polymers currently in commercial production include:

- PLA (polylactic acid) used in packaging
- PDO (1, 3 propanediol) found in textile and carpet fibers
- PHA (polyhydroxy fatty acids) in coatings, film and molded goods
- Starch- and cellulose-based co-products
- Anti-freeze from soybean/corn residues

- Polyethylene from sugar cane
- NOP (natural oil polyols) from soy bean oil in furniture and automotive foams, coatings, sealant and elastomers
- PGR (polyethylene glycol renewable) from biodiesel in boat hulls, bathroom fixtures, antifreezes, heavy-duty liquid laundry detergents

The U.S. DOE considers the following chemicals, which can be produced from sugars via biological or chemical conversion, particularly promising for making high-value hio-based chemicals or materials:

- Four carbon 1,4 di-acids (succinic, fumaric and malic)
- 2.5 furan dicarboxylic acid
- Aspartic acid
- Glucaric acid
- Glutamic acid
- Iatonic acid
- Levulinic acod
- 3 - hydroxy - butyrolactone
- Glycerine
- Sorbitol
- Xylitol and arabinitol

The NREL Biomass Program is involved with six major biorefinery projects that are focused on new technologies for integrating the production of biomass-derived fuels and other products into a single facility. They are:

• **Second Generation Dry Mill Refinery** (Broin and Associates, Inc.) This project will enhance the economics of existing ethanol dry mills by increasing ethanol yields and creating additional co-products.

• **Integrated Corn-based Biorefinery** (E.I. du Pont de Nemours and Co., Inc.) This project will build a bio-based production facility to convert corn and stover into fermentable sugars for production of value-added chemicals.

• **Making Industrial Biorefining Happen** (Cargill Dow LLC National) This project will develop and validate process technology and sustainable agricultural systems to economically produce sugars and chemicals such as lactic acid and ethanol.

• **Advanced Bioefining of Distiller's Grain and Corn Stover Blends** (High Plains Corp.) This project will develop a novel biomass technology to utilize distiller's grain and corn stover blends to achieve significantly higher ethanol yields while maintaining the protein feed value.

• **MBI/USDA** (John Ashworth)

• **New Biorefinery Platform Intermediate** (Cargill, Inc.) This project will develop a biobased technology to produce a wide variety of products based on 3-HP acid, which is produced by fermentation of carbohydrates.

• **Separation of Corn Fiber and Conversion to Fuels and Chemicals** (National Corn Growers Association) This project will develop an integrated process for recovery of the hemicellulose, protein, and oil components from corn fiber for conversion into value-added products.
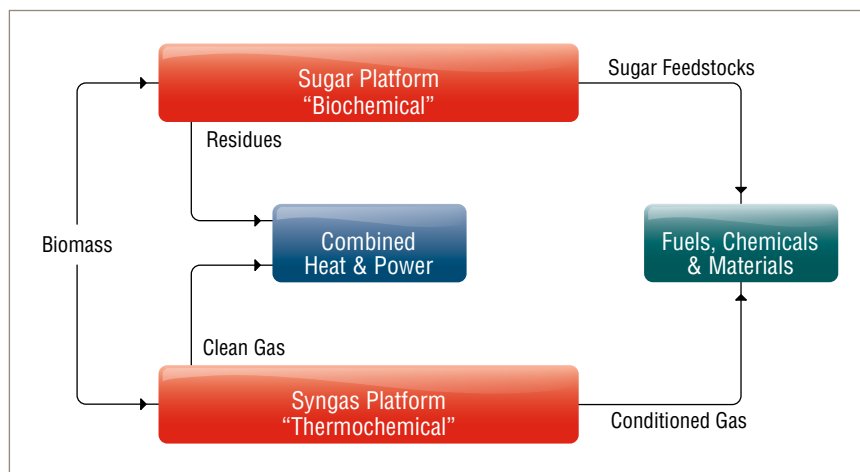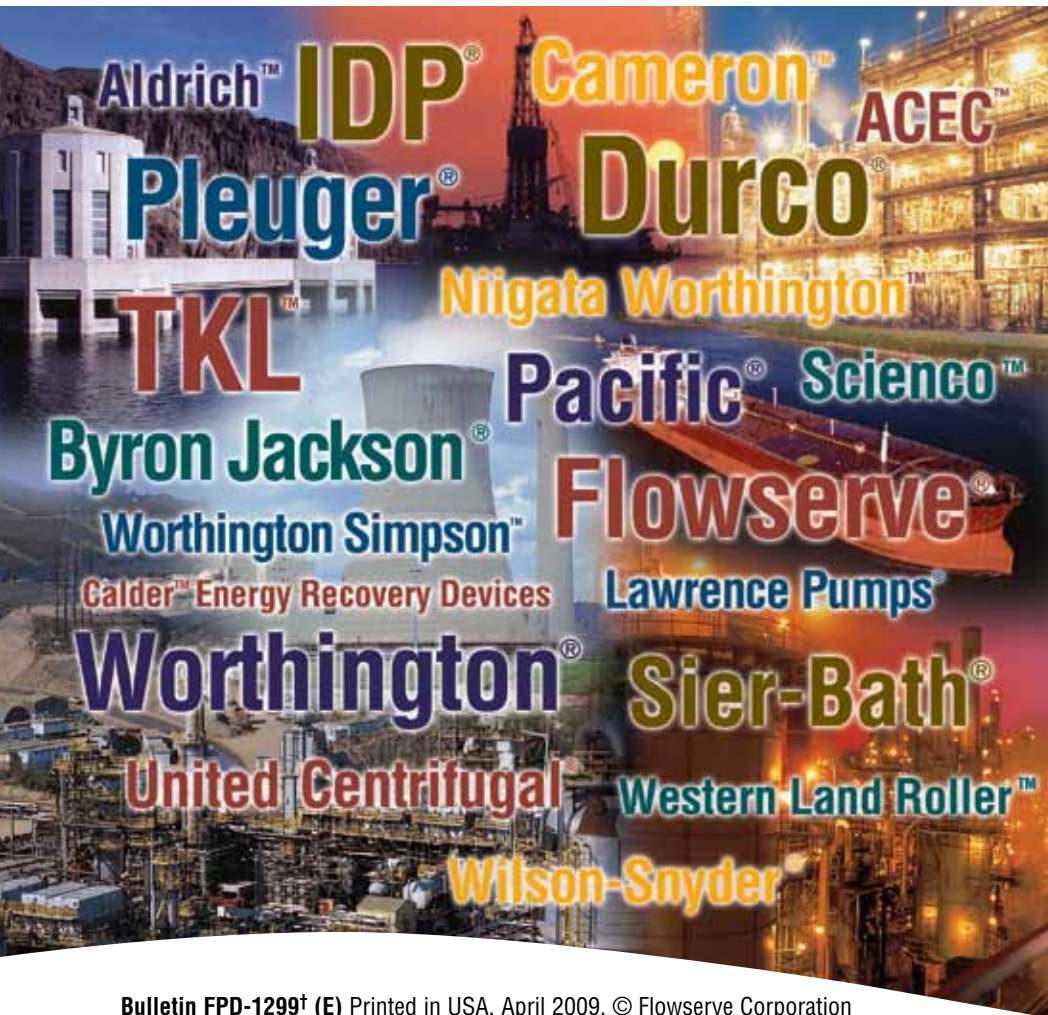
Figure 23 – Biorefinery Concept

Figure 24 – The Biorefinery: Processes and Products

Biomass Feedstock	Processes	Primary Products	Final Products
Wood, grass crops, residues wastes	Hydrolysis (acid, enzymes)	Sugars/lignin	Heat
	Gasification (heat, oxygen)	Synthesis gas	Electricity
	Digestion (bacteria)	Biogas	Fuels (biodiesel ethanol, BTL[1], methane, DME[2])
Feedstock production, collection handling preparation	Pyrolysis (catalyst, heat, pressure)	Bio-oil	Bio-based materials/chemicals, plastics solvents, pharmaceuticals, adhesives, acids, paints, pigments, ink, detergent, etc.
	Extraction (mechanical, chemical, physical)	Carbon rich materials	
	Separation (mechanical, chemical)	Plant products	
	Combustion co-firing	Heat	

1. Biomass to liquid fuel (BTL)
2. Dimethylether (DME)

Notes

Notes

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Byron Jackson®
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