A Review of the Engineering Aspects of the Biodiesel Industry

by

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Preface

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Report Objective

This report was drafted to provide those parties considering investing in the construction of biodiesel plants within Mississippi with some technical insight into the key production issues pertaining to the biodiesel industry. While the content of this report is intentionally technical, the focus was to provide this information at a level that the educated general investment community and government policy makers would be able to gain the most information from a concisely written document.

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Executive Summary

Biodiesel is a fully renewable liquid fuel source that can be used as an alternative to petroleum diesel fuel. The commercial biodiesel industry is a new market with the first consumer biodiesel pump in the US opening in 2001. 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 base (sodium hydroxide). This process is referred to as the Base Catalyzation Process. The production reaction, known as transesterification, results in the volumetric 10:1 production of biodiesel and glycerine. When high levels of free fatty acids are present in the feedstock, then the Acid Catalyzation Process is recommended as an alternative to the Base Catalyzation Method. Free fatty acids form "soap" when processing using base catalyzed transesterification. The most common source of triclycerides used for biodiesel production is plant oils and animal fats. Commonly used lipid feedstocks are soybeans (almost all of the biodiesel made in the US uses soy), canola, sunflower, cottonseed, poultry and beef fats, used cooking oil, and rapeseed (most common feedstock used in Europe). Some promising research is being done on the use of algae or mustard as novel feedstocks. The produced biodiesel during processing is typically water-washed to remove processing residuals. Biodiesel can be used as a neat diesel fuel (100%) or more often within a blend with petroleum diesel. Blending within the US is typically done at a 5% biodiesel blend (B5 Blend) to as high as a 20% biodiesel blend (B20 Blend). The glycerine produced can be used in its crude or refined form and is a key income stream for today's biodiesel industry.

The total US production of biodiesel in 2002 was approximately 20 million gallons with the national biodiesel production capability at that time being about 55 million (about 50% usage of production capability). Additionally, if the entire oleochemical industry within the US was converted to biodiesel production, a little over 100 million gallons of biodiesel could be produced within the US using 2002 figures. The US uses approximately 33 billion gallons per year of diesel fuel. Clearly, total replacement of petroleum diesel is not feasible using today's capability; however, displacement is feasible. Clearly, dramatic increases in production capacity of biodiesel are needed to provide significant displacement potential.

Most of the biodiesel production facilities within the US during the early 2000's were in the 2 million gallon per year production capacity. Construction costs are dependent on plant scale; however, $1 per gallon of annual production capacity is a good rough figure. Production costs are the key factor hindering maturation of this promising fuel. Currently, reported production costs range from a low of $1.60/gallon to a high of $2.40/gallon. Approximately 70% of these production costs are associated with the lipid feedstock.

From a performance standpoint, biodiesel has generally reported to burn within today's diesel engine without any significant problems noted. In fact, many studies report that biodiesel burns much cleaner. The primary problems reported are the cleansing effect that neat biodiesel has on diesel engines causing residuals to clog the fuel filters over the first few tankfulls and decay of rubber lines and gaskets (can easily be replaced with more compatible materials).

Energetically, biodiesel has approximately 85% of the energy potential of petroleum diesel. When blended with petroleum diesel at levels less than 20% (v/v), these blends generally perform similarly to neat petroleum diesel. The US Park Service has adopted biodiesel use at many of its parks within the US and thus has kept an extensive database on the fuel's performance in a wide variety of vehicles. Their data show excellent performance and strong evidence as to the high potential for using biodiesel as a displacement fuel to petroleum. Several original equipment manufacturers (OEMs) are providing warranty coverage for fuels using as much as a B20 fuel blend with more OEMs supporting B-blend usage each year. From environmental performance standpoint, biodiesel burns much more cleanly than petroleum diesel with dramatic reductions in most pollutant levels noted, except for slightly higher NOx levels (up to 5%). In the case of a spill, biodiesel is a fairly environmentally benign chemical that is fully biodegradable. Conversely, petroleum diesel releases into the environmental are a serious threat to the ecosystems receiving these chemicals because many of the components of petroleum diesel are carcinogenic and persistent.

In summary, biodiesel is a promising alternative to petroleum diesel. However, the economic aspects of the industry are hindering further growth. Current production capacities are very small compared to diesel usage within the US. Of key concern is the high cost of production. From a technical performance standpoint, biodiesel blends and neat biodiesel usage should not represent any hindrances to growing the market.

Chapter I: Introduction to Biodiesel and the Biodiesel Business

The Need for Renewable Fuels

The earth contains a wide variety of carbon reservoirs that can be harnessed to meet societal power requirements in the form of gaseous, liquid, and solid fuels, with liquid fuels being of most importance. The modern world has come to rely almost exclusively on fossil-based reserves, a non-renewable resource, for production of liquid fuels. However, the cost and politics of being totally dependent on these reserves is getting progressively more expensive from both a strategic and sociological standpoint. A renewable source of fuels is required for meeting the future energy needs of the United States and the world. Unfortunately, politics and policy tend to be crisis management oriented resulting in a lag in the development of alternative fuels.   The strategic and economic adverse impacts of the United States being so dependent on unstable petroleum reserves has finally pressured the leadership of the United States to pursue domestic resources of energetic products capable of economically and technically supporting the country's energy needs.

To facilitate the development of a renewable production base for liquid fuels in the United States, more and more incentive packages are becoming available to producers and distributors of these renewable liquid fuels. Therefore, the economic environment within the United States is such that numerous states are organizing programs to promote the establishment of economically viable renewable liquid fuels within their respective states. To date, the majority of these efforts have been centered within the Midwestern United States, with some activity appearing within the West and East Coasts. The reasoning behind such a significant push for renewable fuel production within the Midwestern United States is that the primary feedstocks for ethanol and biodiesel (the primary renewable fuels under development) are grown in this area of the country in vast quantities. The two major feedstock crops being corn and soybeans (feeds for ethanol and biodiesel, respectively).

Another aspect to the establishment of a viable renewable liquid fuels industry within the United States is that these chemicals are much more environmentally friendly than their respective petroleum-derived counterparts. This more environmentally friendly aspect holds true for not only the final products, but the feedstocks as well. This benefit is observed from both a potential spill/release scenario as well as improved air emissions, except for the case with NOx compounds associated with biodiesel utilization. The environmental benefits of biodiesel will be discussed in more detail later in this section.

The Chemistry of Biodiesel

Biodiesel, which is produced from plant and animal-based feedstocks, represents an alternative to petroleum-based diesel fuel. This fully renewable resource can be produced from cultivated high oil-yielding plants that are energetically charged from energy derived from the sun and absorbed carbon dioxide.   Animal-based products (fats and oils) are energetically

charged from plants, which also means that they are also ultimately energetically charged from the sun and composed of absorbed atmospheric carbon dioxide because animals directly use plants and thus indirectly use these primary energy and carbon sources.

Chemically speaking, biodiesel is a mixture of mono-alkyl ester of fatty acids obtained from extracted plant oils and/or collected animal fats. Both plant oils and animal fats are commonly referred to as "lipid" feedstocks. Lipids are actually a class of chemicals found in plants and animals (Baum 1982). This class of chemicals is relatively diverse in terms of chemical composition; however, the chemicals within this classification are categorized within this single common grouping due to their solubility within various organic solvents, such as benzene, ether, chloroform, and carbon tetrachloride (often known as "fat solvents"). Lipids are not very soluble in water. They are the primary energy storage system for animals, while plants utilize carbohydrates (starches) as their primary energy storage system. Chemicals classified as lipids include fats and oils, waxes, phosphoglycerides, sphinolipids, glycolipids, steroids, terpenes, prostaglandins, and fat-soluble vitamins. Note that only the first five groups are saponifiable lipids, which means that they can be reacted to form esters (i.e. used to produce biodiesel). Among these chemicals, fats and oils are by far the most abundant lipids. Both are considered triglycerides because they are esters made up of three fatty acids joined to a glycerol molecule (which is a trioxy alcohol). Note that glycerol is also commonly referred to as glycerine.

A lipid is a fat if it is a solid at $25^{\circ}C$; if not, then it is considered an oil. Fats generally come from animal sources and oils come from plants; however, structurally they generally are similar. The primary difference between a fat versus an oil is the fatty acid building block linked to the glycerol. Approximately 70 fatty acids are known to exist. Some contain no double or triple carbon-carbon bonds and are thus referred to as being "saturated". All are straight chained in terms of the carbon skeleton (actually, the carbons are aligned as a zig-zag straight chain). Their basic generalized chemical formula is: $C_nH_{2n-1}COOH$. The most common saturated fatty acids are lauric, myristic, palmitic, and stearic acids. Conversely, the most common unsaturated fatty acids are palmitoleic, oleic, linoleic, and arachidonic acids. Generally, the higher the degree of unsaturation of the fat or oil (the more double bonds), the lower the melting point making unsaturated fatty acids better components for achieving superior cold flow performance (Armstrong, 1989).

When fatty acids react with glycerol, each fatty acid bonds to one of the glycerol carbons, forming a glyceride bond. Figure I-1 shows the chemical structure of glycerol along with a triglyceride with three different esterified fatty acid chains. This type of triglyceride is a mixed triglyceride. The triglyceride in Figure I-1 is called 1-Stearoyl, 2-linoleoyl, 3-palmitoyl glycerol, and it is composed of a glycerol molecule and three fatty acids: stearic acid, linoleic acid, and palmitic acid. Glycerol is composed of a three-carbon chain with an -OH bond on each carbon. Stearic acid is a saturated carboxylic acid with 18 carbons, and palmitic acid is a saturated carboxylic acid with16 carbons. Like stearic acid, linoleic acid is a carboxylic acid with 18 carbons, but it differs from stearic acid in that it contains two carbon-carbon double bonds. Table I-1 shows the formula and structure of each acid. In naming a triglyceride, one of the terminal carbons on the glycerol is picked as the starting point of the triglyceride. Then the fatty acids are listed in numerical order based upon the position of the glycerol carbon that each acid

is attached to. Fatty acids typically end in -ic, and when naming a triglyceride, the -ic is replaced with -oyl. For the triglyceride in Figure I-1, the glycerol carbon to the left is chosen as the starting position, so the first part of the name is "1-Stearoyl." The No. 1 indicates that stearic acid is on the fist glycerol carbon. Linoleic acid is on the second carbon so it is given the name "2-linoleoyl." Palmitic acid is on the third glycerol carbon, so it is called "3-palmitoyl." When the names of these ester bonds are attached to the name of the root molecule (glycerol), the identity of the triglyceride emerges: 1-Stearoyl, 2-linoleoyl, 3-palmitoyl glycerol.

Most oils typically contain on the order of 14 fatty acids. If a quality feedstock is used, the bulk of these acids are bound as part of the triglycerides (Tyson 2001). Most, if not all, feedstocks contain free fatty acids, with the better feedstocks containing very few. The implications of containing high levels of free fatty acids are discussed in more detail later in this document; but, suffice it to state that their presence forms soap during production which poses processing challenges and is of little real value to most parties within the biodiesel industry (however, soap may be further processed into other chemicals that may be of value). As mentioned earlier, triglycerides can contain different types of fatty acids (thereby, they are mixed triglycerides). Fats tend to proportionally contain more saturated fatty acids and plants generally have more unsaturated fatty acids. If all three of the fatty acids are the same, then the triglyceride is known as a "simple" triglyceride. Pure fats and oils are colorless, have no odor, and are tasteless; however, impurities commonly absorbed into the lipid give triglycerides color, taste, and odor. The plant oils commonly used in biodiesel production contain mostly oleic and linoleic acids. Most fats used or proposed for use in biodiesel production contain fairly equal portions of palmitic, stearic, and oleic acids as the dominant fatty acid composition.

Technically, plant oils can be directly used within the diesel engine; however, they have several characteristics that make them less than desirable for this use (primarily due to their high viscosity under most operating conditions). In fact, when Diesel developed his engine, vegetable oils were the fuel that he used to power his early units; however, as petroleum diesel was developed and its production economized, diesel engines were exclusively converted to petroleum derived fuels (Coltrain, 2002). Additionally, vegetable oils have less than desirable characteristics when used directly as a fuel and not transformed into alcohol esters (Canakei and Van Gerpen, 2001; Calais and Clark, 2003). Therefore, conversion of the oils into a better fuel product (biodiesel) has been undergoing further development/optimization over the past several years. Numerous processing techniques, both batch and continuous operations using either base or acid catalyzed reactions, have been tested and proven technically viable. Other techniques are being researched, including lipase induced reactions under development by the USDA (Abigor et al. 2000). However, the base-catalyzed, methyl-transesterification of soybean oil has been the predominant production technique used within the United States. During this process, the soy oil (previously extracted prior to production) is reacted with a primary alcohol (methanol [CH_3OH]) and a base (sodium hydroxide, aka. caustic [NaOH]) to form the fatty acid mono alkyl ester (in this production case, a fatty acid methyl ester which is often referred to as FAME). This production reaction is summarized by the following reaction scheme:

Caustic
Triglyceride + Methanol –> Methyl Ester + Glycerol
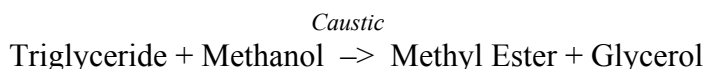
This reaction is classed as the transesterification reaction. This reaction is similar to saponification, which is used to produce soap from fatty acids. On a weight balance basis for the transesterification reaction depicted above, for every 100 pounds of oil/fat and 10 pounds of methanol added, approximately 100 pounds of FAME and 10 pounds of glycerol are produced. This reaction reduces the molecular weight of the triglycerides by 60% when the methyl ester is formed. Additionally, viscosity is reduced eightfold and volatility increases (Environment Canada, 2003). Ethanol can be used in place of the methanol, which would form an ethyl ester instead of the methyl ester produced using methanol (Environment Canada, 2003). Additionally, other bases can be substituted for the caustic, including potassium hydroxide. The transesterification reaction is performed within closed reactors with the alcohol and base added as a single reagent (they are premixed). Actually, the methanol and caustic react to form sodium methoxide, a highly reactive chemical, which breaks apart the triglyceride molecule into the methyl ester and glycerol (Pelly 2003). The transesterification reactor is stirred and often heated to temperatures approaching $60^{o}C$ to accelerate the reaction (some processes are operated at room temperatures). The residence time within a batch transesterification reactor varies from 1 to 8 hours, depending on the composition of the reagents and reactor conditions (MDAC 2003). Recent research does show potential to reduce esterification reaction time due to the introduction of co-solvents which are reported to reduce phase separation of the reagents; thereby, reducing mass transfer limitations (ES&E, 2001).

It is important to note that free fatty acids present within the triglycerides must be monitored to ensure that excessive soap and downstream separation problems are not encountered. Process operations are tailored to specific reagents (chemical composition of the feedstocks and alcohol/base reactants) making continual switching of particularly feedstocks operationally challenging, but not impossible (within reason).   After reacting, two phases are formed, the glycerol and ethanol/alcohol phases, because glycerol has a higher specific gravity and is immiscible in the biodiesel phase. A static gravity settling vessel is often used to separate these phases; however, a centrifuge separator can also be used (pits higher capital cost against the benefits of a more rapid and complete separation).   Once the glycerol phase is separated, the alcohol is then removed from the biodiesel using distillation or flash evaporation. With most processes, the biodiesel is cleaned using one to several water washes. The final biodiesel product must comply with ASTM D 6751 in order to be within "specs".

Outside of reagent purity, the key factors impacting the production of biodiesel in terms of quality, rate, and efficiency include temperature, mixing, catalyst type/concentration, and alcohol to ester ratio (Environment Canada, 2003). The glycerol is collected and can be sold as an industrial feedstock to other processes or refined for sale within the pharmaceutical industry. The biodiesel and alcohol are separated allowing recycle of the alcohol within the plant. The biodiesel collected undergoes further processing for cleanup, consisting of water cleanup, distillation, drying, and filtration.

The type of fatty acids and their respective concentrations found in triglycerides depends upon the feedstock source. Soybean oil is the main feedstock for the biodiesel produced in the United States, but in other parts of the world, different feedstocks are used. In South America, coconut oil is used to produce biodiesel, but in Europe, rapeseed oil is the primary feedstock.

Soybean, coconut, and rapeseed oil are derived from vegetables, so climate heavily influences where these vegetables can be grown. Another feedstock is beef tallow, which is composed of the fat from cattle. To illustrate the differing chemical make-up of three commonly used feedstocks, Table I-2 lists the compositions of soybean oil, coconut oil, and beef tallow based upon the fatty acids that they have in common.

The type and concentration of fatty acids in a feedstock are directly related to several key properties in the resulting biodiesel. Conventional diesel fuel consists of long-chain, unbranched hydrocarbons. One of the major reasons biodiesel is a suitable substitute for conventional diesel is the fact that biodiesel consists of long, unbranched chains of fatty acids. One of the most important characteristics of any diesel fuel is its cetane number, which is a measure of the ignition quality of a diesel fuel. The ignition quality is directly related to the ignition delay of the fuel, and the shorter the ignition delay time, the higher the cetane number. Therefore, a high cetane number indicates good ignition quality. Long-chain, unbranched, saturated hydrocarbons have high cetane numbers while branched hydrocarbons and aromatic compounds have low cetane numbers. However, too high or too low of a cetane number can result in incomplete combustion in both cases. Most engine manufacturers recommend a cetane number between 40 and 50 (Knothe et al., 2003). If a feedstock is mainly composed of fatty acids that are saturated, then the cetane number of the biodiesel derived from that feedstock could be too high. Likewise, if a feedstock is mainly composed of fatty acids that are highly unsaturated, then the cetane number could end up being too low. Two other important properties are cloud point and heat of combustion. Cloud point is the temperature at which a fuel becomes cloudy due to the formation of wax crystals, and these crystals can clog fuel lines and filters (Knothe et al., 2003). The heat of combustion is the amount of heat that is released when a certain amount of a material burns. Both cloud point and heat of combustion are directly related to the level of saturation and the number of carbons in a fatty acid. In general, as a fatty acid becomes more saturated or if the number of carbons in a fatty acid chain increase, then cloud point and heat of combustion increase. Therefore, the fatty acid composition of the feedstock plays a vital role in determining the feedstock's suitability for biodiesel production.

It is important to note that the FAME is 100% biodiesel. When directly used as fuel without blending with petroleum diesel, the pure biodiesel is often referred to as "neat" biodiesel. However, most often, biodiesel within the general marketplace is sold as a petroleum diesel/biodiesel blend. These blends are compositionally identified within the marketplace using the "B" designation, which defines the volumetric biodiesel composition of the blend by placing the percentage composition immediately after the letters "B". For example, a 20% biodiesel/80% petroleum diesel is designated as a B20 blend. It is important to note that the USEPA and USDOE both classify B20 diesel as an alternative fuel. Biodiesel should not be confused with the developing fuel, ethanol-diesel blends (E-Diesel), which do not contain biodiesel, but do contain ethanol (which is also a biofuel). As a point of note, McCormick and Parish (2001) present more information on the developing E-Diesel market.

Typically, petroleum and biodiesel are blended using splash blending upon which the biodiesel is poured onto the petroleum component due to the slightly higher specific gravity (SG) of the biodiesel (Tyson, 2001). Recirculated pumping can be used to facilitate mixing if

improper splashing was performed or concerns over poor mixing exist. Liquid fuels temperatures during mixing should be above 50°F.

Overview of Current and Developing Biodiesel Feedstocks

This section presents some introductory issues regarding feedstocks. Note that Chapter II of this report presents a much more thorough discussion on this topic. Since production of biodiesel requires a triglyceride feedstock, many sources of fats and oils have and/or can be used to produce a high quality product. The selection of the feedstock(s) is likely the most critical process decision to be made due to the fact that feedstock cost typically represent 60 - 80% of total production costs (Environment Canada, 2003). Additionally, the long-term availability of the feedstock is another consideration when selecting process reagents. Plus, consideration on how a growing biodiesel market impacts the future cost of the feedstock (and the glycerol) must be taken into account during business plan development.

Within the United States, soy oil is by far the most common feedstock. This is not surprising when considering that soy oil represents approximately 75% of the total poundage of plant oils produced in the United States on an annual basis. In descending order, the top agricultural plant oils produced on an annual basis within the United States as reported by Pearl (2002) are soy (18.3 billion lbs.), corn (2.4 billion lbs.), cotton seed (1.01 billion lbs.), sunflower (1.0 billion lbs.), and peanuts (0.22 billion lbs.). In Europe, rapeseed is the predominant feedstock used (Environment Canada, 2003; IA State, 2003). Commonly accepted biodiesel feedstocks include the oils from soy, canola, corn, rapeseed, and palm. New plant oils that are under consideration include mustard seed, peanut, sunflower, algae, and cotton seed (Peterson et al., 2001; Majewski, 2002).

In the case of animal fats, this feedstock is often called "yellow" grease. Grease collected from cooking establishments is called "brown" grease; however, this source can be made up of both plant and animal derived triglycerides. The most commonly considered animal fats include those derived from poultry, beef, and pork. The largest animal fat producing states are Texas, Iowa, Nebraska, and Kansas (Coltrain, 2002). Pearl (2002) reports that the total animal fats production within the United States is approximately 12 billion pounds per year. It is reported by the MDAC (2003) that approximately half of the existing biodiesel plants within the United States can easily switch from oils to fats and vice versa without any real "hard-pipe" modifications to the plant. Iowa State University (2003) estimates that if all oils and fat produced on an annual basis within the United States were used to produce biodiesel, this would represent only 15% of the total amount of petroleum diesel used on an annual basis within the United States. This is why the issue of finding new alternative feedstocks, such as fats, is essential to proving the ability of biodiesel to meet the energy needs of the United States. One key concern with the use of fats, particularly brown grease, is the potential presence of larger quantities of free fatty acids which during esterification are simply converted to soap, which has to be removed via water washings (Donovan et al. 1998). This is not to say that brown grease should not be considered (particularly in light of their relatively cheap cost), just more carefully evaluated prior to selecting it as a feedstock. In fact, due to worldwide concerns over Mad

Cow's Disease, the availability of rendered greases is likely to increase dramatically thus further reducing prices (ES&E, 2001).

Biodiesel produced from soy oil tends to have a bright gold color. Typically, when animal fats are used as feedstocks, the color of the final product tends to be dark to reddish brown, yet no difference in performance has been reported.

There are other impacts of feedstock selection that can affect production and/or performance. Canola oil is reported by Alcantara et al. (2000) to have a higher sulphur content than other plant oils, which may adversely impact its selection due to pending sulfur emissions requirements. Brown greases require more processing and reaction time than the other feedstocks due to their relative lower level of purity compared to most other feedstocks and more refractory nature to the processing reactions.

The Biodiesel Industry

The production of biodiesel is truly an industry at its infancy within the United States. Although, the chemistry behind the process has been known for many years, the established market associated with petroleum diesel, consumer concerns over technical performance, and the high cost of the feedstocks have resulted in the slow development of a viable biodiesel market within most of the United States. As discussed above, petroleum reserves are finite and becoming economically and strategically costly. Promotion and education of both the consumer and engine manufacturers (referred to as original equipment manufacturers [OEMs]) have begun to broaden the acceptance of biodiesel, and with more much more success, the BX diesel blends. It is generally accepted that B20 can be directly used as a petroleum diesel replacement without any long-term concerns toward engine performance and stability (MDAC, 2003).

The consumer market for biodiesel was literally started only two years ago in 2001 (REN, 2001). During May, 2001, two filling stations began offering biodiesel to consumers. One of these two landmark facilities is located in San Francisco, CA (operated by Olympian, Inc.) and the other in Sparks, NV (operated by Western Energetics Cardlock Biodiesel Industries). As a point of note, the Nevada facility is selling biodiesel that is produced from brown grease collected from the Las Vegas Area. This initiative was provided via a contract from the City of Las Vegas, The Las Vegas Water District, and Clark County Health Department. It is estimated that the total annual production will be over 1 million gallons.

As stated earlier, feedstock costs are the single largest roadblock to the widespread development of a biodiesel industry within the United States. Technological advances in improved crops (increased oil production per acre and reduced cultivation cost), oil extraction efficiency, and reduced processing costs, along with the discovery and use of alternative feedstocks (such as fats), have improved the outlook for the biodiesel industry. However, finding profitable markets for the glycerol produced and the supply of sufficient quantities of cost appropriate feedstocks continue to plague the industry. As petroleum costs rise and the government provides incentives to the fuels market, coupled with further technological breakthroughs, the biodiesel industry should continue grow at a similar to more rapid pace,

unless a better replacement for petroleum diesel is discovered (which does not appear likely at this time).

The United States government has attempted to grow the biodiesel market by including biodiesel use within the Energy Policy amended 1998 (MDAC 2003). This has resulted in a growing user base that includes the US Postal Service and the US Park Service. Experts expect the United States production of biodiesel to reach 2 billion gallons per year by 2010 (US DOE, 2003). The European Union projects the biodiesel market share in Europe to exceed 5% of total diesel use by 2005 (Alcantara et al. 2000).

Coltrain (2002) reported that there are over 200 transportation fleets within the United States already using biodiesel blends as their fuel source. He also states that as of 2002, that US biodiesel production facilities are capable producing over 60 million gallons per year; however, only 10% of this capacity appears to have been utilized to actually produce biodiesel (University of Missouri-Rolla, 2003). This is a dramatic growth given that in 1999, only 1 million gallons of biodiesel was produced within the United States. Given the total estimated production capacity of the oleochemical industry, he estimates the current total biodiesel production capacity of the United States to be approximately 200 million gallons per year, if all facilities were converted to biodiesel production. One particularly promising statistic is that biodiesel usage within the United States increased over 40% in Year 2002 to over 12 million gallons (Chemical Market Reporter, 2002). Within Europe, diesel is the fuel of choice for many more consumers than the United States. Coltrain (2002) reports that Germany uses the most biodiesel with over 750 million gallons burned in 2002. Most of this biodiesel was rapeseed derived.

Two longer-term strategies may be used for growing the biodiesel market. The first defines biodiesel as a replacement for petroleum based diesel. This option theoretically provides a fully renewable source of fuel for the United States economy; however, the facts are that there is nowhere near enough production capacity today within the United States to meet current usage demands. Additionally, the higher cost of biodiesel, based on today's production economics, would likely have an adverse impact on the overall United States economy, impacting all aspects of industrial production from agriculture to consumer goods due to increased transportation costs. A more realistic approach from a holistic marketing of biodiesel viewpoint appears to be the blending of the biodiesel into petroleum fuels. This approach provides displacement of petroleum diesel, which responds to the national energy goal of reducing foreign oil dependency and moving toward renewable sources. The production capacity within the United States does appear to have potential to meet the demands of this option.

Another interesting aspect of growing the biodiesel market involves the establishment and maintenance of "niche" markets. Several of these markets have begun to be established within the United States. Examples include development of a user base among "green-minded" consumers, supply contracts to government agencies and government/private fleets, and sale of the product as a marine diesel fuel (due to its much lower environmental threat upon release within water bodies). Other options include selling biodiesel as an additive to petroleum based fuels to improve certain characteristics, such as lubricity. The U S Navy is currently considering converting most of its land and sea-based diesel fleets to JP-8, a jet fuel that is very similar to petroleum diesel. However, one key concern is that JP-8 has a low lubricity. Blending with

biodiesel may offer a good option to address this concern, while increasing the usage of renewable fuels. This concept does have a slight flaw in that the overall concept of converting to JP-8 is to reduce fuel supply management within the Navy into one liquid fuel as a means of streamlining logistics. Adding biodiesel provides another dual-fuel logistical problem, except that the volume of biodiesel would be much smaller than today's fuel strategy of supplying both jet fuel (aircraft) and petroleum diesel (small hulls and land vehicles). Planners at the University of Missouri-Columbia (Weber et al., 2003) propose an interesting market development strategy that focuses on "community-sized" biodiesel hubs. This approach involves producing and using biodiesel within agricultural/industrial hubs. The production capacity that this group evaluated was in the 500Kgal per year range. Their economic evaluation provides some evidence that this concept may be feasible; however, significant planning, agreement, and long-term commitment among all involved parties appear to be absolute requirements if this concept will have both economic and social merit.

A major milestone for the biodiesel industry was the announcement by Green Star Products Inc. on February 24, 2003 that the largest biodiesel production facility in the United States will be constructed in Bakersfield, CA (Green Star Products, 2003). This facility will have a production capability of 35 million gallons per year. This is a significant undertaking when considering that the total biodiesel actually produced in 2002 was only 15 million (production capability was near 60 million).

Production Energy Balance of Biodiesel versus Petroleum Diesel

The total fossil energy ratio for biodiesel production has been estimated by the USDOE and USDA to be in excess of 3.2, while petroleum diesel was reported to be only slightly greater than 0.8 (Sheehan et al., 1998). Total fossil energy ratio is an estimate of the amount of fossil fuel equivalents used for production over the total fossil fuel energy equivalents delivered by the product. In terms of vehicular mileage ratings, both neat biodiesel and B20 blends are reported by the Biodiesel Board to have lower power ratings (petroleum diesel and biodiesel have thermal values of 131,295 and 117, 093 BTUs/gallon, respectively [US Biodiesel Board, 2003]). It is interesting to note that neat biodiesel has more energy potential than neat ethanol: approximately 120,000 BTUs/gallon versus 80,000 BTUs/gallon for ethanol (Coltrain, 2002); however, neat biodiesel has approximately 10% less energy on a volumetric basis than petroleum diesel (Tyson, 2001).

Performance of Biodiesel Within Diesel Engines

Biodiesel and biodiesel blends should only be used within compression ignition engines (diesel burning engines) that meet the specs as defined by ASTM D 975 (Tyson, 2001). Numerous formal studies and a multitude of performance experience have been accumulated by a variety of sources. Kalam (2002) states that biodiesel will reduce engine life slightly when used in its pure form. However, the costs to the user of this slightly reduced engine life may be

offset by the cost of having to implement techniques to reduce engine emissions. Additives have been researched that can reduce engine wear when using neat biodiesel. B20 has been shown to reduce engine life at about the same rate as ordinary diesel, while still providing the benefits of lower emissions and decreased petroleum demand (Kalam, 2002). In fact, discussions with parties having used significant quantities of B100 state that the engines upon inspection are cleaner internally and in fact seem to perform better. Biodiesel has a higher lubricity which is a positive characteristic in terms of extending engine life (Clean Air Fleets, 2003). The only reported exception to this appears to be the degradation of seals and hoses after extensive use of neat biodiesel (Majewski, 2002). Studies of elastomer compatibility with biodiesel indicate that nitrile rubber, nylon 6/6, and high density polyethylene were affected by long-term contact with biodiesel. However, no impacts were noted when biodiesel was contacted with Teflon and the vitons, 401-c and GFLT. SeQuential Fuels Inc. (Eugene, OR) does recommend that all fuel-contacting rubber components within diesel engines that will start burning neat biodiesel products be replaced with more compatible parts. They also recommend keeping a spare fuel filter on board because biodiesel tends to clean up dirt and carbon deposits within the fuel storage/delivery/burn systems; particularly, for the first few tankfulls.

One key concern over biodiesel usage has been the potential inability of biodiesel blends to perform well within cold climates. Clean Air Fleets (2003) reports on the experience of a commercial fleet operating out of Cedar Rapids, IA where the operational data was collected over the course of an extraordinary cold winter period. Using a B20 mix, Five Seasons Transportation Inc, report no problems with performance over the course of 1.4 million miles of operation by its fleet. There are several commercial additives that can be used to reduce problems associated with cold weather use.

OEMs have been slow to approve biodiesel usage within their warrantied engines. Most OEMs to date have only approved B5 blends (Majewski, 2002). Their main concern involves the degradation of the biodiesel via oxidation which increases the amount of free water and contamination thus adversely impacting engine performance and longevity. Most experts state that biodiesel should be stored for periods less than six months, making over-production and storage difficult unless longer stability can be developed (see Chapter VI for more details). Some OEMs have approved use of neat biodiesel within their engines and therefore offer biodiesel warrantees. These companies include Caterpillar and John Deere. However, equipment operators are strongly encouraged to contact their respective OEM and/or equipment service provider to determine performance and warrantee specifications concerning the use of biodiesel products within their equipment

Table I-1. Fatty Acids of 1-Stearoyl, 2-linoleoyl, 3-palmitoyl glycerol (McMurry, 2000)
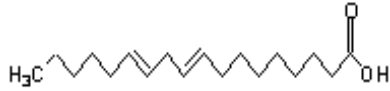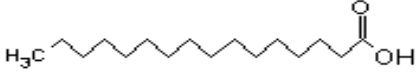
Acid	Chemical Formula	Structure
Stearic	$CH_3(CH_2)_{16}COOH$	
Linoleic	$CH_3(CH_2)_4CH\!=\!CHCH_2CH\!=\!CH(CH_2)_7COOH$	
Palmitic	$CH_3(CH_2)_{14}COOH$	

Table I-2. Fatty Acid Composition of Several Feedstocks (Ma and Hanna, 1999)

Fatty Acid	Soybean	Beef Tallow	Coconut
Lauric	0.1 wt. %	0.1 wt. %	46.5 wt. %
Myristic	0.1 wt. %	2.8 wt. %	19.2 wt. %
Palmitic	10.2 wt. %	23.3 wt. %	9.8 wt. %
Stearic	3.7 wt. %	19.4 wt. %	3 wt. %
Oleic	22.8 wt. %	42.4 wt. %	6.9 wt. %
Linoleic	53.7 wt. %	2.9 wt. %	2.2 wt. %
Linolenic	8.6 wt. %	0.9 wt. %	0 wt. %
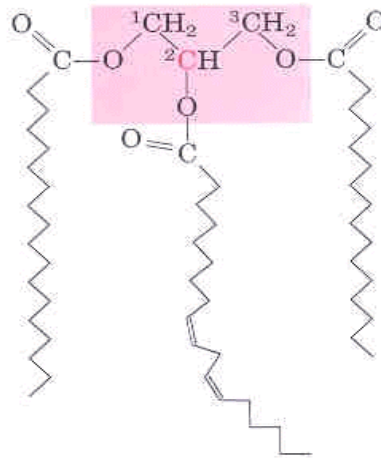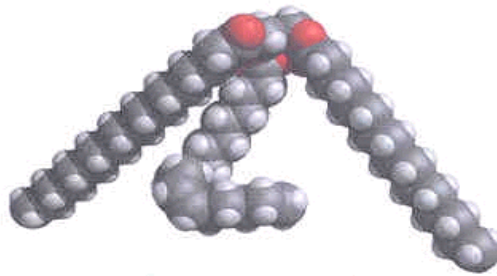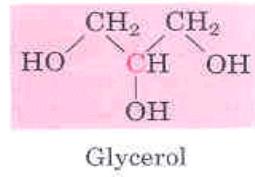
Figure I-1. Chemical Structure of Glycerol and a Typical Triglyceride (Nelson and Cox, 2000)

Chapter II: Feedstock Issues

Presently, biodiesel is produced using vegetable oils, animal fats, or used cooking oil. National biodiesel production in 2001 was approximately 20 million gallons. Projections are that 100 to 500 million gallons per year will be produced over the next few years with the actual production amount being dependent on future energy policies (AIM-AG, 2002). Most of the biodiesel was used to prepare B20, a mixture of 20% biodiesel (balance petro-diesel). Numerous studies have demonstrated that unmodified diesel engines operating with B20 perform cleaner and with similar power compared to those operating with petro-diesel. The reported Mississippi diesel consumption in 2000 was 330 million gallons. Thus, blending petro-diesel with 20% biodiesel could potentially generate a 66 million gallon biodiesel market in the state. Mississippi's agriculture includes a variety of vegetable oil feedstocks that could be used to fulfill local and/or regional future supply for biodiesel production. Mississippi ranks 3rd, 4th, 11th, 16th, and 21st among states in production of cotton, rice, sorghum for grain, soybeans, and corn for grain, respectively (MASS, 2002). Additionally, the state ranks 4th, 23rd, and 30th, in production of broilers, cattle and calves, and hogs and pigs, respectively (MASS, 2002). Animal rendering facilities, especially the poultry industry, could provide inexpensive feedstock (yellow grease) for biodiesel production and minimize price variability in vegetable oil feedstocks that could be caused by increases in their demand

Table II-1 presents the 2001 Mississippi production yields of agricultural commodities and corresponding estimated biodiesel yields estimated from these quantities as feedstocks. The table clearly shows that soy beans and yellow grease represent the largest potential biodiesel feedstocks in Mississippi followed by rice, corn, and sorghum. State production of soybean and yellow grease is very localized. Soybeans are cultivated mostly in the north western part of the state, while yellow grease is produced mostly in the central counties. This factor has to be taken into consideration when siting a biodiesel production facility.   Transportation costs are minimized if the biodiesel facility is established in close proximity to the feedstock. Implementation of crop rotations could facilitate the utilization of other commodities for biodiesel production. For example, corn can be rotated on a yearly basis with soybean and cotton. Reports consistently indicate 10-25% yield advantages for cotton or soybeans grown in rotation with corn on Mississippi farms (MAFES, 2003).

Technical constraints in terms of seed preparation have to be considered during design of an oil extraction facility capable of producing high quality refined oil from different feedstocks. Each of the feedstocks presented in Table II-1 requires different seed management techniques and transportation to a central oil extraction facility from remote parts of the state would be costly.

Feedstock Extraction Techniques

In developing countries, the extraction of oil is carried out mostly by pressing methods; whereas pressing followed by solvent extraction is commonly employed in developed countries

(Salunkhe et al., 1992). Pressure extraction can leave behind an undesirably high oil content that results in a low quality meal (and waste of oil). Pressure extraction can result in a meal with 5 to 6% oil content. In contrast, solvent extraction yields meals with 1 to 2% residual oil.

Similar seed preparation procedures are conducted prior to solvent or pressure extraction (Snider, 1990). Seeds are stored under clean and low temperature and moisture (<13%) conditions to avoid spoilage. Prior to extraction, seeds are cracked into several pieces and the hulls (if any) removed by blowing air. Separation of the hulls results in more space in the extractors for the oil bearing tissue. The cracked pieces are conditioned with steam to enhance oil extraction and converted into flakes by putting them through smooth rollers. Small flakes are associated with higher oil extraction efficiency. However, flakes thinner than 0.01 inch can clog the extraction system (Snider, 1990). Therefore, an optimum flake size that results in relatively high oil extraction yield and minimizes total costs has to be determined in field operations.

The flakes can be fed to pressure or solvent extractors. During pressure extraction, the flakes are fed into a screw device rotating within a horizontal heavy steel cage. As the flakes enter at one end of the cylinder, they are subjected to high pressures between the rotating screw and the stationary cage. The pressure forces oil through openings in the cage, while the residual press cake is carried horizontally in the direction of the shaft and is discharged at the other end of the cylinder. The capacity (60 tons/day) of these systems is small compared to solvent extraction (4,000 tons/day) (Snider, 1990). Additionally, the oil extraction efficiency is lower. The higher amount residual oil in the meal can become rancid and unacceptable for animal feed. One advantage of pressure extraction over solvent extraction is its versatility to simultaneously handle a variety of seeds.

Solvent extraction is the preferred oil extraction alternative for large scale operation in developed countries. Figure II-1 illustrates a solvent extraction process. Hexane is currently the most commonly used extraction solvent for oil seeds used throughout the world because it is cheap ($0.07/lb) and abundant. The flakes and hexane are fed to an extractor unit counter currently to maximize mass transfer efficiency. The hexane is continuously recovered from the oil in a series of evaporator/condenser operations. Solvent is removed from the defatted flakes by steam injection in a device called a meal-desolventizer, which also heats the flakes to inactivate compounds, such as trypsin inhibitors, essential to nutritional value. The flakes are then cooled and ground to the correct particle size for feed mixing.

Once the oil has been extracted, it is further refined to produce oil with the desired chemical and physical properties. Figure II-2 presents typical oil processing steps for the production of refined oil. First, the crude oil from the extraction unit is degummed to remove phospholipids or lecithin. These compounds are removed because they are insoluble and precipitate out of the oil during storage forming a viscous mixture that is difficult to manage. Gums are removed by water washing followed by centrifugation. The recovered gum or lecithin is a valuable by-product and is used by the food industry as an emulsifier and anti-sticking agent (Snider, 1990).

Free fatty acids form soaps during the biodiesel production processes that use base-catalyzed transesterification, resulting in a more difficult separation of the biodiesel/glycerol mixture. Free fatty acids can be removed via caustic treatment during oil refining or converted to alkyl esters using acid catalyzed transesterification (discussed in more detail in the next

chapter of this report). However, the relatively small amount of free fatty acids in vegetable oils makes the latter non-practical. Thus, free fatty acids in vegetable oils as feedstock for biodiesel are removed by washing with a dilute solution of sodium or potassium hydroxide followed by centrifugation. The free fatty acids may be recovered for soap manufacture or added to the meal.

Pigments and remaining traces of gums, free fatty acids, and minerals are removed by bleaching, which is done by adding specially mined clays to the oil. The clays adsorb the unwanted materials and are separated from the treated oil by filtration. Valuable oil is adsorbed along with the unwanted materials, but normally recovery of this oil is not cost effective (Snider, 1990). The bleaching clay is discarded after one treatment.

Many vegetable oils have small quantities of waxes that solidify and cause cloudy oil at low temperature. Waxes are removed by cooling the oil to 43 to 46 °F, crystallizing the waxes (4 hours), and carefully heating the oil to 64 °F before filtering to separate the wax crystals from the liquid oil (O'Brien, 1998). Utilization of non-dewaxed oils with relatively high wax content for biodiesel production, such as corn, canola, and sunflower, could result in biodiesel that performs poorly at low temperatures. Wax deposits can be formed in the fuel tank and/or injection system, resulting in long term severe engine damage.

A deodorization step is conducted in the food industry prior to oil shipment to remove volatile compounds that may adversely affect odor and flavor. However, this refining step is not necessary when the oil is a feedstock for biodiesel production.

Yellow Grease Refining

Waste fats from meat packing industries are classified as yellow grease. The proteinaceous material contained in yellow grease is removed by steam distillation followed by bleaching and filtration. During steam distillation, proteins turn black and require bleaching for removal. Filtration removes traces of moisture and impurities. One important characteristic of yellow grease regarding biodiesel production is its high free fatty acid content (approximately 15%). A two step acid/base catalyzed biodiesel production is required to handle the high free fatty acid content in yellow grease. The acid catalysis step converts the free fatty acids into alkyl esters. Removal of free fatty acids from yellow grease prior to base catalysis avoids excessive soap formation, which occurs if the free fatty acids are allowed to react with hydroxide or alkoxide bases. Additional alkyl esters and glycerol are produced during base catalyzed transesterification of the remaining triglycerides in yellow grease.

Correlation of Feedstocks with Biodiesel Chemical and Physical Properties

Biodiesel produced from yellow grease has a relatively high pour point value compared to that produced from vegetable oils. The pour point is indicative of biodiesel flow properties at cold temperatures. A high value could limit biodiesel utilization in cold weather regions. The pour point temperature is directly correlated with the oil or fat composition. Animal fats have a high content of saturated fatty acids and a relatively high pour point value. In contrast, fatty

acids in vegetable oils are mostly unsaturated and yield biodiesel with better cold weather performance. Table II-2 compares oil composition of potential feedstocks for biodiesel production in Mississippi, including yellow grease. It can be observed that oil from seeds contain over 70% unsaturated fatty acid composition compared to approximately 50% for yellow grease.

A chemical property that also is correlated with the fatty acid composition of the feedstock is the cetane number. This property is a measurement of a fuel's ignition quality. High cetane numbers contribute to easy cold starting and low idle noise. Studies show that cetane number increases with longer chain fatty acids and more saturated molecules (Van Gerpen et al., 1995). Thus, biodiesels produced from yellow grease is higher cetane numbers compared to those produced from vegetable oils.

These correlations of feedstock fatty acids compositions and biodiesel chemical and physical properties indicate that there is a fatty acid composition that results in an optimum cetane number and cold flow characteristics. Either yellow grease or soybean oil will yield biodiesel that meets ASTM standards for diesel fuel and excellent performance in Mississippi during the four weather seasons.

Technology Shortcomings

Present technology for biodiesel production and processing results in an excellent quality alternative fuel that complies with ASTM standards for petro-diesel. The main problem with biodiesel over the last 20 years has been the high production costs caused by high priced feedstocks. For example, most of the biodiesel is generated using soybean oil as the main feedstock. Soybean oil is the least expensive commercial vegetable oil (~$0.20/lb). It takes 7.3 pounds of soybean oil to produce 1 gallon of biodiesel. Thus, feedstock cost alone is at least $1.50/gallon of soy biodiesel. Furthermore, as biodiesel utilization increases the demand, and consequently, the price of soybean oil will increase. Figure II-3 illustrates the relationship between cost per gallon of biodiesel and feedstock cost per pound. The figure indicates that biodiesel begins to be cost competitive with petro-diesel when the cost of feedstock is approximately $0.10 per pound or less and production reaches 10 million gallons per year. Presently, only yellow grease meets this price constraint.

One alternative to positively transform the economic feasibility of biodiesel is the synthesis of other value added products. Fatty acid methyl esters can be transformed into useful chemicals and raw materials for further synthesis (Schuchardt et al., 1998). Alkanolamides, fatty alcohols, and sucrose polyesters are just some of the products that can be generated from fatty acid methyl esters, with markets already existing in the plastics, pharmaceutical, and cosmetics industry. A biorefinery concept has to be implemented to generate revenue from other growing markets in addition to biodiesel.

Table II-1. Mississippi Agricultural Commodities and Potential Biodiesel Production

Commodity	Production[1]	Unit	Gallons of Biodiesel
Corn	50,050,000	bushels	4,062,500[+]
Soybeans	36,960,000	bushels	26,400,000[++]
Rice	16,445,000	cwt	4,271,428[*]
Cotton	2,396,000	bales	16,892,734[**]
Sorghum	7,134,000	bushels	1,660,276
Broiler Production	4,078,400,000	pounds	52,966,234[#]

[1]Reference (MASS, 2002)
[+]One bushel of corn yields 1.6 pounds of corn oil (www.iowacorn.org)
[++]One bushel of soybeans yields 1.4 gallons of biodiesel (USDA, 2002)
[*]Assuming 10% bran is recovered from the rice paddy and bran contains 20% oil.
[**]Assuming 60% cotton seeds are recovered during ginning and cotton seeds contain 18.85% oil.
[#]The rendering process generates 0.10 pounds of fat/lb of animal (Shumaker et al., 2000)
Except for corn and soybeans, it was assumed that 7.7 pounds of oil yields one gallon of biodiesel.

Table II-2. Composition of Oil from Mississippi Feedstocks

Fatty Acid	Feedstocks					
	Cotton Seeds**	Soybeans**	Rice Bran[+]	Corn**	Sorghum[#]	Yellow Grease**
C-12:0						0.1
C-14:0	0.7	0.1	0.49	0.1		3.2
C-14:1						0.9
C-15:0						0.5
C-16:0	21.6	10.6	13.80	10.9	14.0	24.3
C-16:1	0.6	0.1		0.2		3.7
C-17:0				0.1		1.5
C-17:1		0.1				0.8
C-18:0	2.6	4.0	2.01	2.0	2.1	18.6
C-18:1	18.6	23.3	43.60	25.4	31.0	42.6
C-18:2	54.4	53.7	36.60	59.6	49.0	2.6
C-18:3	0.7	7.6	1.17	1.2	2.7	0.7
C-20:0		0.3	0.91	0.4		0.2
C-20:1						0.3
C-22:0		0.3		0.1		

[#]Food and Agriculture Organization of the United Nations, 1995
**O"Brien, 1998
[+]Salunkhe et al., 1991

Figure II-1. Hexane Solvent Extraction (Hass et al., 2002)

Crude
Vegetable
Oil

↓

Degumming

↓

Caustic
Refining

↓

Prebleach

↓

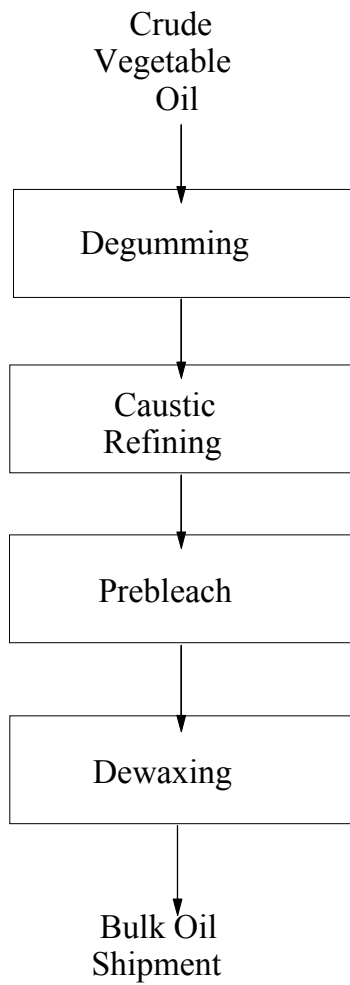Dewaxing

↓

Bulk Oil
Shipment
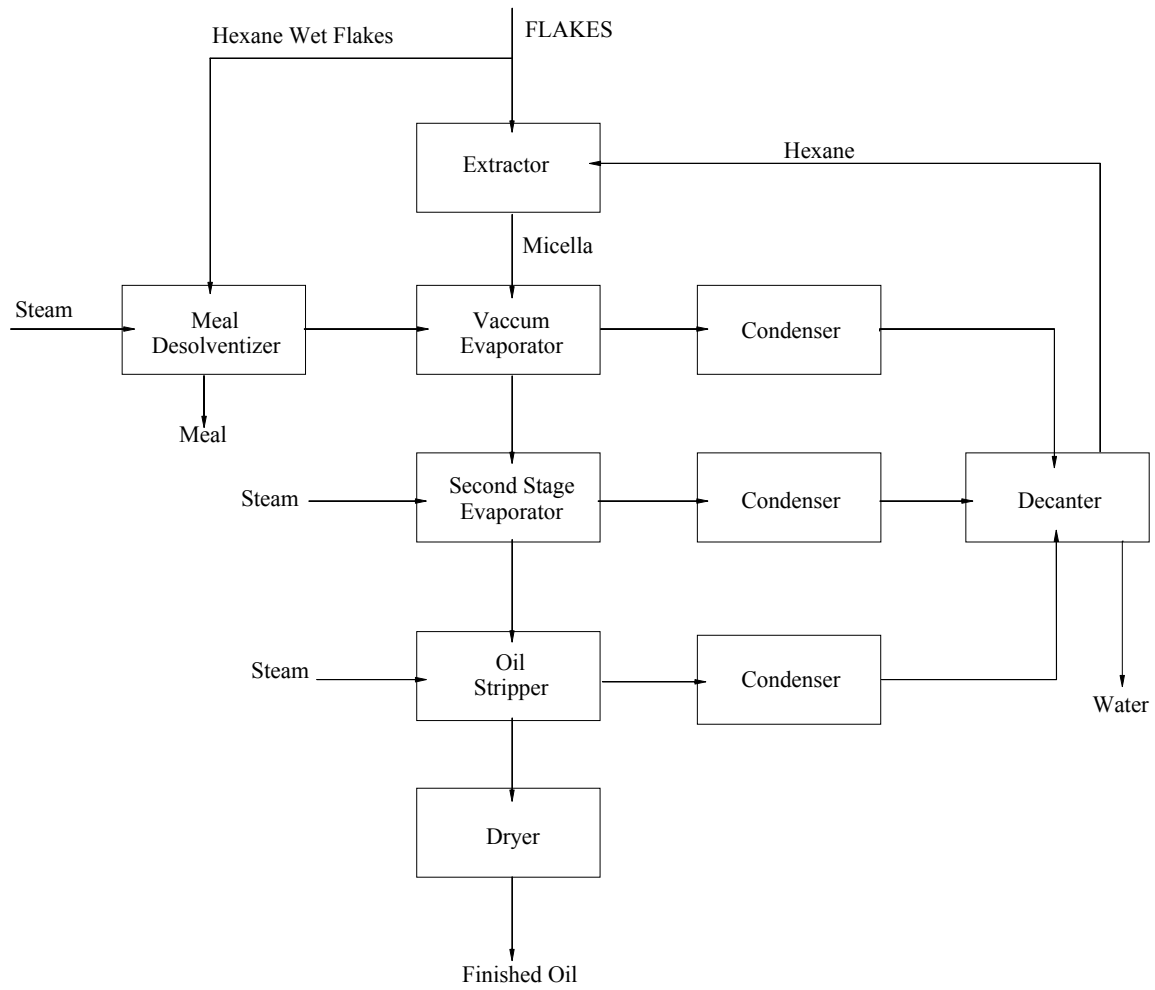
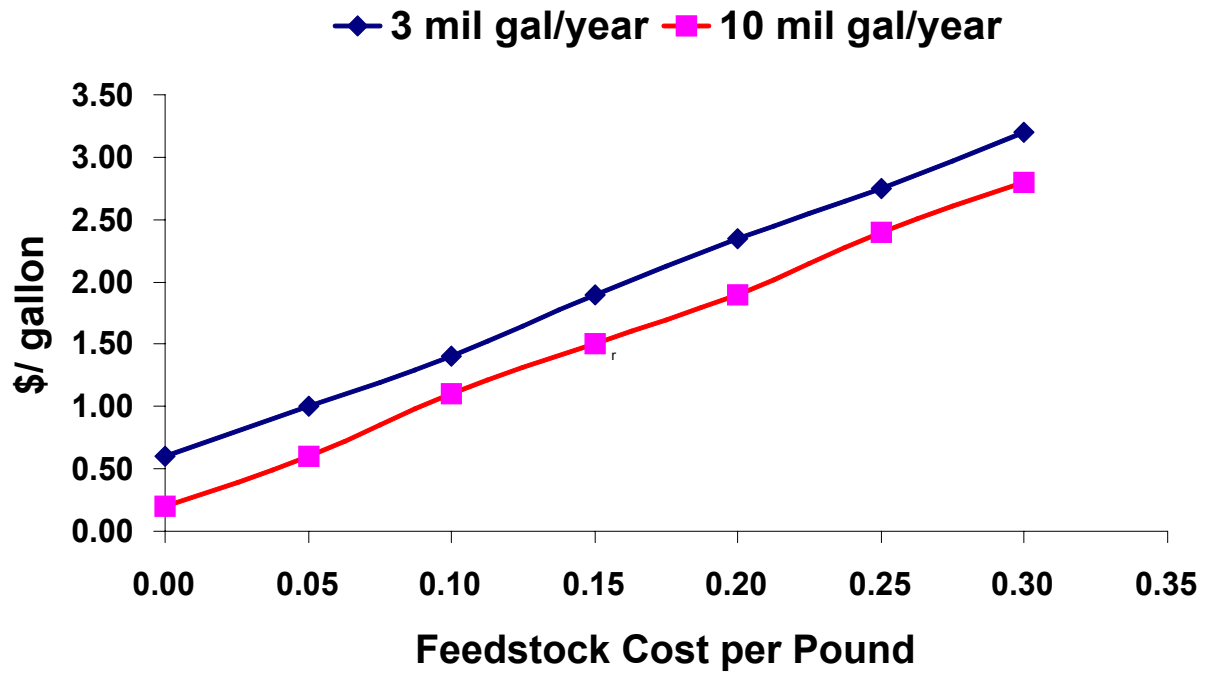**Figure II-2. Crude Oil Refining Steps (O'Brien, 1998)**

Figure II- 3. Theoretical Production Cost Per Gallon of Biodiesel (Tyson, 2002)

Chapter III: Production of Biodiesel

Base Transesterification

As introduced in Chapter I, 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 glycerol (Majewski, 2003). The typical form of the reaction is illustrated in Figure III-1 where the short chain alcohol is methanol (CH_3OH), and R^1, R^2, and R^3 represent the fatty acid chains. Transesterification reactions can be either base-catalyzed or acid-catalyzed, but base catalysis is often preferred because it is more rapid than acid catalysis (Knothe et al., 2003). Base-catalysis is also viewed as being economically superior over acid-catalysis based on the following (NBB, 2003):

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

In base-catalyzed transesterification, alkaline catalysts such as sodium hydroxide (NaOH) and sodium methoxide ($NaOCH_3$) are used. In a study by Freedman et al., the optimum conditions for forming alkyl esters were the following (Freedman et al., 1984):

- The feedstock should be a refined oil with a free fatty acid content of less than 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
- For laboratory use the catalyst should be 0.5% sodium methoxide, but for large-scale reactions the catalyst should be 1% sodium hydroxide 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 (C_2H_5OH), and butanol (C_4H_9OH) at 60°C, 75°C, and 114°C for 1 hour. Even at 32°C, vegetable oils can be 99% transesterified in about 4 hours with an alkaline catalyst (Freedman et al., 1984).

For base-catalyzed transesterification to be successful, the free fatty acid content should be less than 0.5% and the short chain alcohol should be moisture free. Free fatty acids are carboxylic acids that have not been esterified. Whenever more free fatty acids are present, more alkaline catalyst can be added to compensate for the increased acidity, but this also results in the formation of soap that causes an undesirable increase in viscosity or the formation of gels that

interfere with separation of the alkyl esters from glycerol (Freedman et al., 1984). When free fatty acids react with short chain alcohols, one of the products is water. Therefore, the amount of water formed increases with free fatty acid content during base-catalyzed transesterification. As little as 0.3 wt. % water can reduce yields because the water consumes the alkaline catalysts to produce soap, so the moisture level must be restricted (Freedman et al., 1984; Veggiepower, 2003).

Figure III-2 shows a block flow diagram (BFD) of a typical base-catalyzed transesterification process. 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 (Freedman, et al., 1984). Once the reaction is complete, the products are allowed to separate. The biodiesel layer will settle on top of the glycerol 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 the biodiesel, it can be mixed slowly with water using several methods such as bubble or mist washing (Greentrust, 2003). When water is added to biodiesel, an aqueous phase forms below the biodiesel because water is more dense and the two materials are immiscible in each other. With the bubble washing method, air is introduced into the aqueous layer where bubbles form, and these bubbles float up into the biodiesel layer. As the bubbles pass through the biodiesel, they carry a film of water that absorbs impurities, such as unreacted methanol and alkali soaps. When the bubbles reach the surface, they burst and release the water, which passes back through the biodiesel layer and absorb impurities for a second time (Veggiepower, 2003). Once the water reaches the aqueous layer, the concentration of impurities is distributed over a larger volume of water, and the water is bubbled back through the biodiesel again. If necessary, the wash water can be drained off, and fresh water can be added. The advantage of bubble washing is it requires less water than the other wash methods (Green Trust, 2003).

The mist washing system uses a fine mist of water that is sprayed onto the top of the biodiesel phase. The mist absorbs impurities as it passes through the biodiesel (Green Trust, 2003). Misting does consume more water than bubble washing because the wash water does not have the dual cleansing ability of going up and down.

Once washing is complete, biodiesel is heated to the point that any remaining water and alcohol evaporate out of the mixture, leaving the biodiesel behind. To reduce raw material expenses, 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 glycerol layer along with some of the unreacted methanol. Depending upon the amount of free fatty acids and soap present, the glycerol may need to be purified. As mentioned before, the water reacts with catalyst to form soap, which is basic (pH>7). If the level of soap is high, then the pH of the biodiesel and glycerol may be too high; thus, requiring adjustment. To compensate for this, an acid such as tannic acid or acetic acid is added to lower pH (Pelly, 2003). After adding mineral acid to the glycerol layer, a sequence of distillation, settling, and evaporation can be used to separate the glycerol from the fatty acids and the methanol. The glycerol can be sold as items such as saponification crude (88% purity) or soap lye crude (80% purity) (Weber and Van Dyne, 2003). Soaps can also be recovered and sold as industrial-use items such as degreasers (Pelly, 2003). Figure III-3 depicts

a process flow diagram (PFD) of base-catalyzed transesterification. This particular process flow diagram is adapted from Canakci et al.   This process typically has a yield of about 95% biodiesel when using soybean oil. Therefore, about 0.95 lbs of biodiesel are formed per pound of feedstock. In Canakci's development of a pilot-scale biodiesel plant, the following conditions are used:

- The feedstock is stored in a cone-bottom vessel at room temperature
- A pump transfers the feedstock to the main reaction tank, which is stainless steel and equipped with an explosion-proof mixer that has a fixed speed of 1750 rpm
- A 6:1 molar ratio of alcohol to feedstock is used, and the amount of reactants are measured by a load cell that is mounted on the reaction tank
- If the alcohol and catalyst are purchased already mixed together, then they are stored in a tank until they are needed, but if the alcohol and catalyst are purchased separately, then they should be mixed together
- The alcohol-catalyst mixture is added to the reaction tank using an air-operated pump
- The reactants are agitated for 8 hours, and then the mixture is transferred to a cone-bottom tank for glycerol separation and ester washing
- Separation of the phases can be observed in as quick as 10 minutes and can be complete within two hours after stirring has stopped. However, complete separation of the phases can take as long as 20 hours
- In the work by Peterson et al., the washing process is described in detail. After the phases separate, water is added at the rate of 5.5% by volume of the feedstock and then stirred for 5 minutes (Peterson, et al., 2003). Canakci's research shows that warm water at approximately $60^{o}C$ is more effective at removing soap and free glycerol from the esters than cold water
- Once the glycerol settles again, it is removed from the ester layer and sent to the glycerol storage tank
- A delicate two-step process is used to wash the esters. A water wash solution is added to the esters at rate of 28% by volume of oil along with 1 gram of tannic acid per liter of water in order to neutralize the pH
- After the water-acid solution is added to the esters, the components are gently agitated
- Using the bubble washing method, air is carefully introduced into the aqueous layer while agitation is still occurring. This process is continued until the ester layer becomes clear
- Then the aqueous solution is drained from the esters, and water is added at 28% by volume oil for a final washing. The waste wash water can be recycled to the fresh wash water feed. The esters are then filtered with 20-micron cellulose filters as they are being pumped to the external storage tanks
- Biodiesel should be stored in clean, dry dark containers to prevent contamination. The containers should be isothermal to prevent exposure to temperature extremes.

Proper materials of construction for the containers include aluminum, steel, fluorinated polyethylene, fluorinated polypropylene, and Teflon. Materials such as copper, brass, lead, tin, and zinc should not be used as these materials are easily corroded by biodiesel (NBB, 2003)

- Glycerol should be stored in a closed container that is in a cool, dry, and well ventilated area that is free of contaminants (SafeTec, 2003)
- A load cell measures the amount of glycerol, washing water, and ester product
- A density meter installed at the exit of the separation tank identifies the glycerol, water, and ester interfaces during the separation

Other Transesterifications: Acid Catalysis and Integration of Base and Acid Catalysis

The base-catalyzed transesterification processes described above are suitable for feedstocks with low free fatty acids; however, not all feedstocks have a low free fatty acid content. When the free fatty acid content is greater than 1%, the base-catalyzed reaction described above does not work very well. Therefore other methods of transesterification must be used. One method that has been researched is acid-catalyzed transesterification. Acid catalysis 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; however, acid catalysts have been found to be effective in converting free fatty acids into esters (Canakei and Van Gerpen, 2003). 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. The basic idea behind the two-step process is that by reducing the free fatty acids to a low level (less than 1%) by acid catalysis, the quicker base catalysis method could be used to actually convert the triglycerides to biodiesel. Figure III-4 illustrates the reaction that occurs in the pretreatment process.

With acid catalysis, methanol is most often used, but any short-chain alcohol will suffice. The products of the reaction are methyl esters, water, unreacted sulfuric acid, and any triglycerides that may have been in the feed. In the work by Canakci et al., an acid-catalyzed pretreatment section was added to the pilot-scale plant previously described. Figure III-5 shows the process flow diagram of the pretreatment unit coupled with a base-catalysis unit.

Operational Details on Acid Pretreatment

The operating parameters of Canakci's pretreatment process are presented in this section. High free fatty acid feedstocks such as yellow grease or brown grease are stored in a heated, agitated, cone-bottom storage tank. Once in the tank, the feedstock is kept at approximately 55-60°C using a heater. The purpose of these conditions is to prevent solidification. The agitation is provided by a recirculating pump. Since yellow grease and brown grease can have meat and bone particles in them, a 20-micron cellulose filter is used to remove the insoluble materials. A pump moves the feedstock to the stainless steel pretreatment reaction tank, and a load cell

measures the weight of the feedstock that is transferred to the reaction tank. Once the alcohol solution with acid catalyst is prepared, the mixture is added to the pretreatment reaction tank using an air-operated pump. If yellow grease is used, then the first pretreatment should use 5% sulfuric acid by weight and a 20:1 molar ratio of alcohol to feedstock. If brown grease is used, the first pretreatment should use 10% sulfuric acid by weight and a 20:1 molar ratio of alcohol to feedstock. Brown grease requires a higher concentration of sulfuric acid because of the higher level of free fatty acids. Agitation is provided by a pump. The mixture temperature is maintained at 60°C by a heat exchanger installed in the process loop. While in the pretreatment reaction tank, free fatty acids react with the esters, and one of the products in this reaction is water, which will form a separate phase from the esters. If the water is not separated from the pretreated material, then further reactions will be inhibited because water will consume the alkaline catalyst in the transesterification section. After about 1 hour, the first step of the pretreatment has reached steady state. Then the reactants are transferred to a stainless steel settling tank that is used to separate the methanol-water mixture from the feedstock. After a residence time of 24 hours, the methanol and water will rise to the top of the tank. At this point, the methanol and water are in a single phase and can be removed to a waste tank. Then distillation can be used to separate the methanol-water mixture, and the methanol can be recycled through the process. A pump transfers the feedstock from the first pretreatment settling tank back to the pretreatment reaction tank, and additional methanol-acid mixture is added. For the second pretreatment of yellow grease, 5% by weight sulfuric acid should be used along with a 40:1 molar ratio of alcohol to feedstock. If brown grease is used, the second pretreatment should use 10% by weight sulfuric acid and a 40:1 molar ratio of alcohol to feedstock. Once again, the required concentration of sulfuric acid is greater for brown grease because of higher free fatty acids. A pump is used to recirculate the mixture for 1 hour at 60°C, and then that same pump transfers the mixture to a stainless steel tank for a second settling process. At this point in the process, the free fatty acid content is less than 1%, and the pretreated feedstock is transferred from the second pretreatment settling tank to the main reaction tank. Since the feedstock no longer has a high level of free fatty acids, the feedstock can be converted to biodiesel using the same base-catalyzed transesterification method as before. One of the biggest advantages of Canakci's design is that both low free fatty acid and high free fatty acid feedstocks can be used and at the end of the process, the two sources of biodiesel can be mixed and stored together.

Continuous Flow Plants

Canakci's biodiesel plant is a batch process because the reactants are not continuously flowing during conversion. Biodiesel plants that generate less than 10 million gallons of biodiesel per year are typically batch processes; however if production is greater than 10 million gallons per year, then a continuous process is desirable (University of TN-Knoxville, 2003). Batch facilities require a lower capital investment than continuous biodiesel plants, but are more costly to operate per unit of biodiesel. The study by Peterson et al. gives an example of a continuous process which is illustrated in III-6 (Peterson et al., 2002). The reactants used in Peterson's study were canola oil, ethanol, and potassium hydroxide as the alkaline catalyst. Tap

water was used as the washing material. The equipment required for this process includes the following:

- Two continuous flow centrifuges
- Storage containers for the oil feedstock, biodiesel, and glycerol
- Metering pump
- Hydraulic motor-driven centrifugal mixing pump
- Oil metering pump
- Oil flow meter
- In-line static mixers
- Needle valve
- Gasoline flowmeter
- Polyvinyl chloride tubing

This process begins with oil being metered into the centrifugal mixing pump, and at the same time, the metering pump controls the flow of alcohol-catalyst mixture into the centrifugal mixing pump. The reactants are mixed with high shearing action and then allowed to pass through a series of static mixers before going into the retention network. This network is made of polyvinyl chloride tubing and acts as the reaction vessel for this process. Once the reaction has proceeded, the biodiesel-glycerol mixture passes through another series of static mixers, and mist washing is used to purify the biodiesel. Then the products pass through another series of static mixers before being separated in the centrifuge. The advantages of using a continuous process as compared to a batch process include reduced production cost and time and more biodiesel produced per unit labor. Also, at an oil flowrate of 22.8 L/hr, the continuous flow system produces as much biodiesel in 41.5 hours as one batch from an existing 945 L per batch system, assuming the typical batch takes one week to completely process (Peterson et al., 2002). However, one of the problems encountered with the centrifuge system is the leakage of alcohol vapors, which can be harmful to people. If the process is not built in a well ventilated area, then an alcohol vapor capture system should be installed.

$$CH_2OCOR^1$$
$$CHOCOR^2 \quad + \quad 3CH_3OH \quad \xrightarrow{\text{catalyst}} \quad CH_2OH \quad \quad CH_3OCOR^1$$
$$CH_2OCOR^3 \quad\quad\quad\quad\quad\quad\quad\quad\quad CHOH \quad + \quad CH_3OCOR^2$$
$$CH_2OH \quad\quad CH_3OCOR^3$$
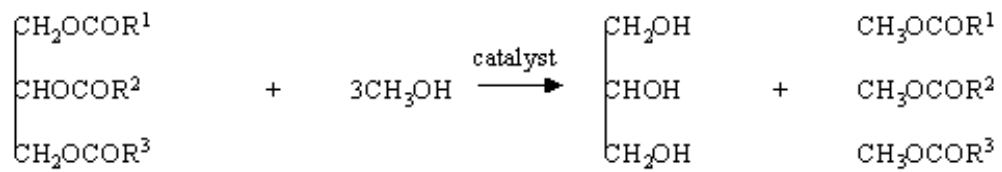
Figure III-1. Transesterification Reaction (Boocock et al., 1996)
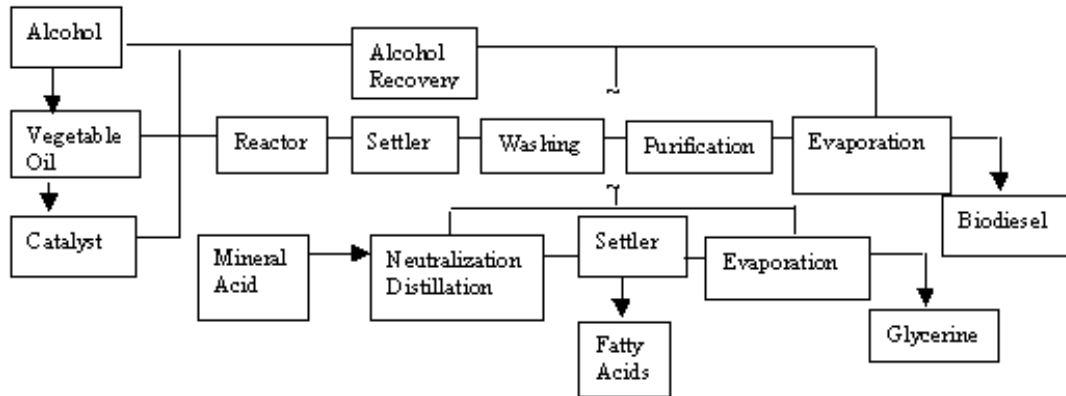
Figure III-2. Base-Catalyzed Transesterification PFD
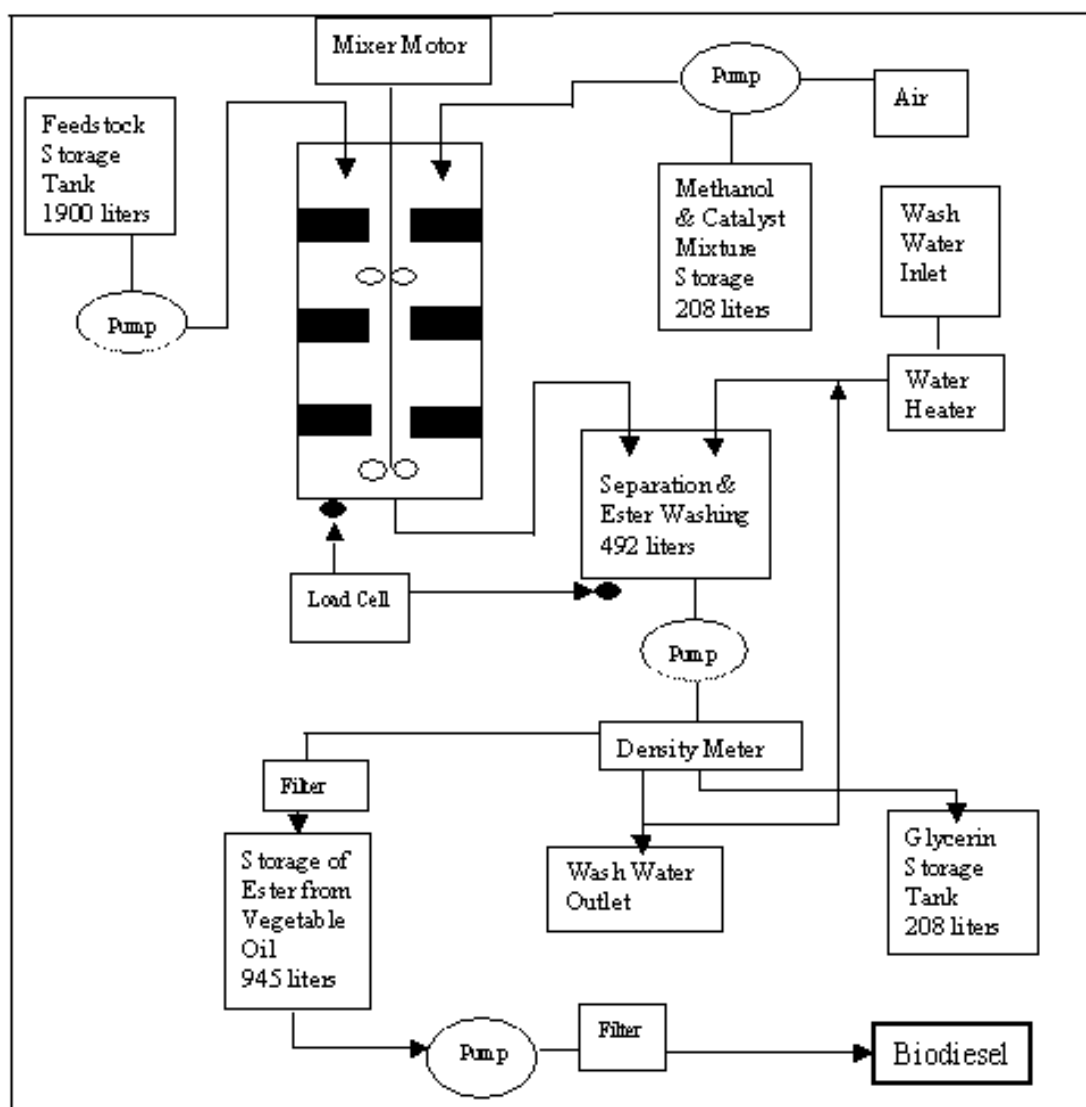
Figure III-3. Base-Catalyzed Transesterification PFD (Canakei and Van Gerpen, 2003)

Free Fatty Acids
+
Methanol
+
Sulfuric Acid
+
Triglycerides (if any)

$\longrightarrow$

Fatty Acid Methyl Esters
+
Water
+
Sulfuric Acid
+
Triglycerides (if any)

Figure III-4. Acid-Catalyzed Pretreatment Reaction (Tyson, 2002)

**Figure III-5. PFD of Pretreatment Unit with
Main Reactor Unit (Canakei and Van Gerpen, 2003)**
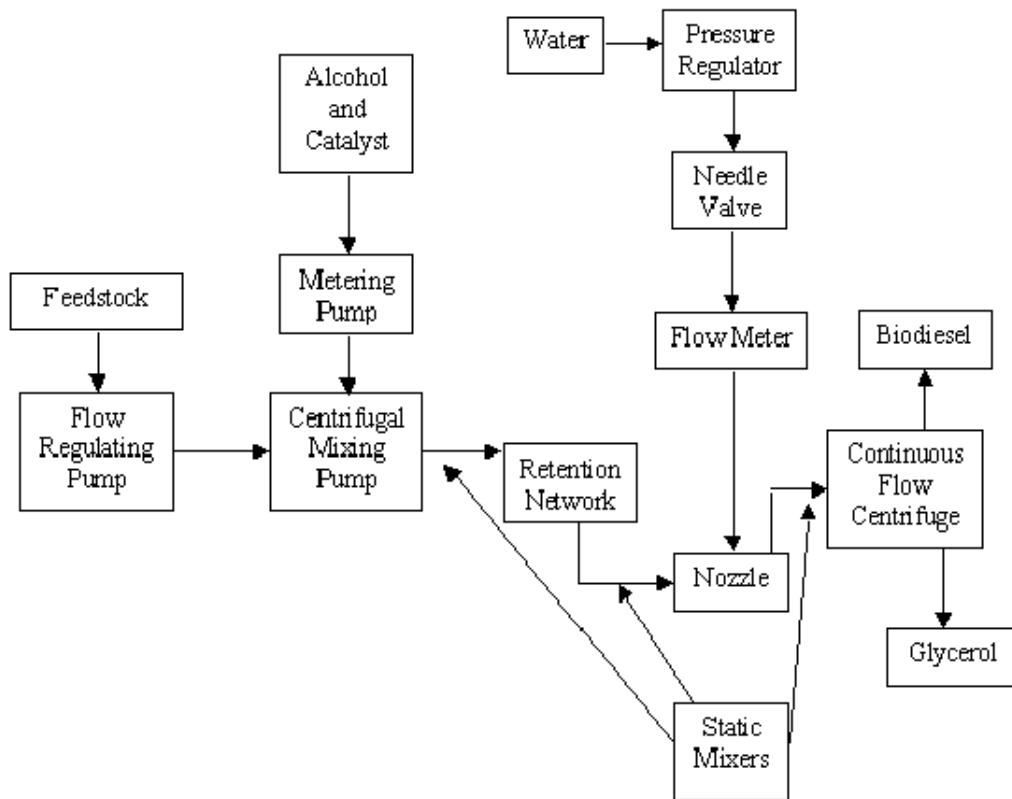
Figure III-6. Continuous Biodiesel Production Process (Peterson et al., 2002)

Chapter IV: By-Products and Wastestreams Produced During Biodiesel Production

Like most other production processes, biodiesel production generates wastestreams; however, unlike many production processes, biodiesel production also makes by-products that are of significant market value. In fact, the economic viability of today's biodiesel industry is so sensitive that the overall economic viability is highly dependent the market price of these by-products. This chapter presents a listing of the major chemicals/products us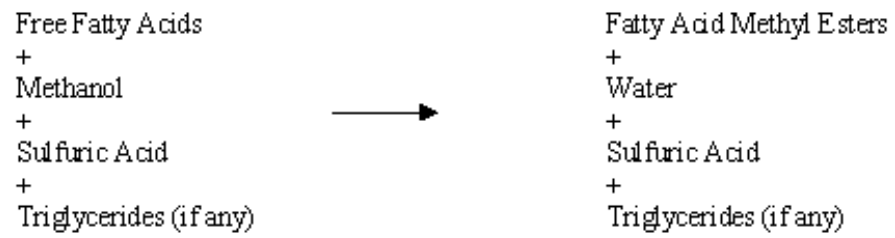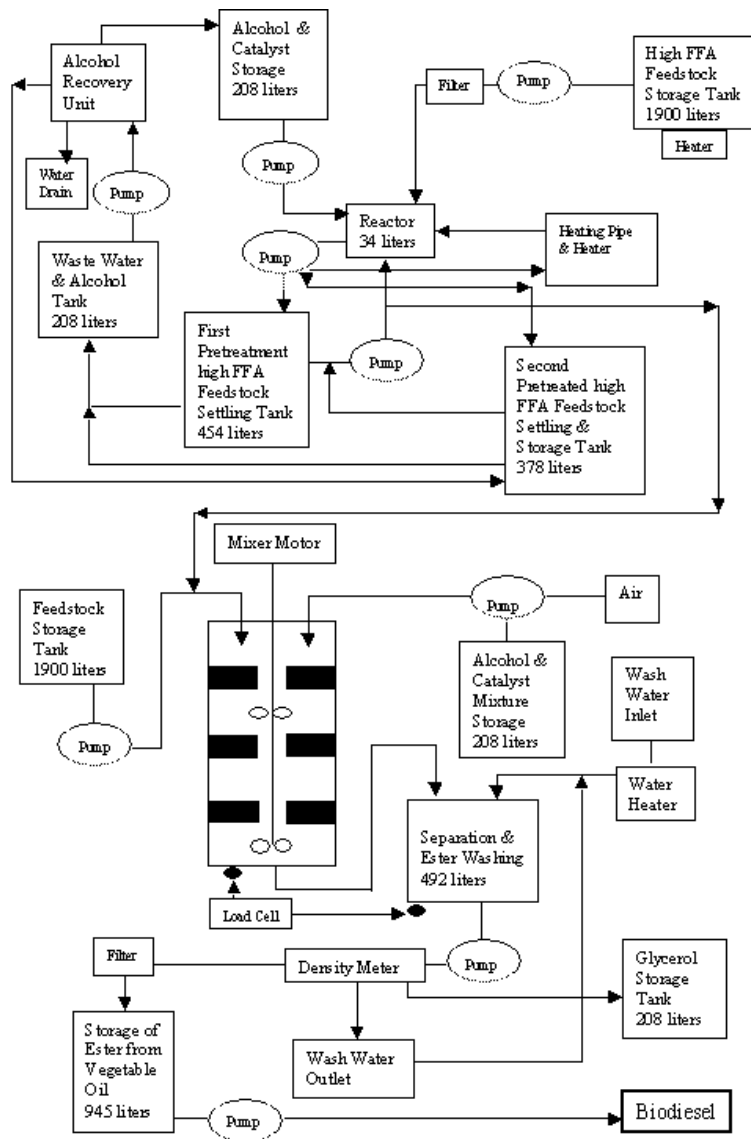ed within the biodiesel process (except the oil which is discussed in detail in this report in Chapters I and II). Also, included in this chapter are by-products, both value-added and waste, that are produced.

Biodiesel

Chapter I presents a detailed description of biodiesel and Chapter III discusses production processes; however, a brief overview of biodiesel is presented for benefit of review for the reader. From 100 pounds of oil and 10 pounds of methanol, the process produces 100 pounds of biodiesel and 10 pounds of glycerol. Biodiesel is a renewable energy source made from biological sources, such as vegetable oils and animal fats. It can be used in its neat form (100% biodiesel, also known as B100) or in a blend with petroleum diesel. The most common blend is B20, or 20% biodiesel and 80% petroleum diesel. Biodiesel is biodegradable and non-toxic, and does not contribute to global warming (Ma, 1999). Petroleum diesel, a fossil fuel, releases carbon into the biosphere that has not been there for millions of years, which, along with the burning of other fossil fuels, has raised the level of "greenhouse gases" in the atmosphere significantly (NREL, 1998). Since the carbon involved in biodiesel is from a biological source, it is already a part of the earth's carbon cycle, and therefore, does not contribute to this greenhouse effect.

Since biodiesel can be operated in almost all diesel engines, it offers an immediate displacement of petroleum. Either B100 or B-blends could be used in a wide variety of applications including trucks, heavy equipment, city bus fleets, freight trains, and generators. Research is currently being done regarding several different areas of fuel consumption, including the blending of biodiesel with jet fuels to reduce emissions (Dunn, 2001). The city of Seattle is currently testing biodiesel in 20 of their garbage trucks. Within the automotive business, one of the keys to selling a product is showing the public it is capable of speed. Many alternatively fueled cars are notoriously slow. However, a publicity-oriented automobile called "The Veggie Car" is powered by 100% biodiesel, and capable of speeds up to 120 mph. This proves to the casual consumer that this new fuel does not mean power must be sacrificed in order to help out the environment. Similar performance and immediate engine compatibility make it convenient for current users of petroleum diesel to switch to something more environmentally friendly. See Chapter VI for an overview of the economic issues pertaining to biodiesel from both an investment and usage prospective. Also, the reader is reminded that Chapter I presents an overview of the biodiesel industry,

Glycerol

Glycerol in its pure form, is a sweet-tasting, clear, colorless, odorless, viscous liquid. It is completely soluble in water and alcohols, slightly soluble in many other common solvents and insoluble in hydrocarbons. Liquid glycerol boils at 290° C under normal atmospheric pressure. Its specific gravity is 1.26 and its molecular weight is 92.09. It is a relatively stable compound and is considered flammable. Until after World War II, nearly all commercial glycerol was produced as a by-product in the manufacture of soap or from the hydrolysis of fats and oils. Today, substantial amounts of synthetic glycerol are prepared from propylene. Crude glycerol is purified to make various grades, such as dynamite grade, yellow distilled, and chemically pure glycerol. Only the highest grades of glycerol are used in foods and medicines (David, 1996).

The profitable glycerol market is very important to maintaining sound economics in the biodiesel process. While biodiesel is the primary product of the process, prospective buyers must also be found for the secondary product, glycerol. High purity glycerol has many potential customers in the world marketplace, including the pharmaceutical and cosmetics manufacturers as well as several others. Industrial chemicals such as CP glycerol, USP glycerol, and dynamite glycerol are all potential markets for high-grade glycerol (Ma, 1998). Glycerol is widely used as a solvent, as a sweetener; in the manufacture of dynamite, cosmetics, liquid soaps, candy, liqueurs, inks, and lubricants. It is also used to keep fabrics pliable, as a component of antifreeze mixtures, as a source of nutrients for fermentation cultures in the production of antibiotics, and in many aspects of medicine. Glycerol can be used as a lubricant in situations where an oil would fail. It is recommended for use in oxygen compressors because it is more resistant to oxidation than mineral oils. Cosmetic, food, and pharmaceutical manufacturers may use glycerol instead of oil for a lubricant, especially if the products come in contact with the lubricant. Glycerol is also used as a humectant in tobacco products. In processing tobacco, glycerol makes up an important part of the casing solution, which is sprayed onto the tobacco before the leaves are shredded and packed. When processing chewing tobacco, glycerol adds sweetness and prevents dehydration. It is also used as a plasticizer in cigarette papers.

Separation of glycerol from biodiesel is relatively simple. Centrifuging after the reaction is finished or even gravitational settling are both sufficient at accomplishing a good separation, depending on how fast the separation is to be completed and the purity of glycerol desired. See Chapter V for much more detail concerning the production of biodiesel and glycerine. Glycerol typically sells for between $0.72 and $1.02 per pound, depending on purity (CMR, 2003).

Meal

Soybean meal is the primary residual left over from the beans after the oil has been extracted. This meal has a high value as a product due to its many potential customers. The meal can be sold as a protein source for food, as fertilizer for the soybean fields, or many other

uses (Biocycle, 2003). Finding a market for the meal is very important. However, this should not be difficult, since the meal associated with this process is in high demand (NREL, 1998).

Recently, the market for soybean meal has grown as demand for new sources of protein for both human and animal consumption has steadily increased. With this heightened demand for soybean meal, soybean oil supply has outpaced demand. The biodiesel process not only provides a market for excess soybean oil, but it takes advantage of the already lower cost of the oil. This is a benefit not only to the biodiesel process, but also to the farmers selling their crop.

The oil extraction step employed is very important in ascertaining the potential customers for the soybean meal. If the more efficient solvent extraction is used, then the meal can only be used for animal feed or fertilizer for crops. However, if pressure extraction is used, the meal can be used as an added value product as a food ingredient. Soybean meal sells for around $190 per ton (CMR, 2003).

Lecithin

Lecithin is used widely in foods as an emulsifier, stabilizer, and antioxidant. Its chemical name is phosphatidylcholine, which identifies its major components of choline, phosphoric acid, glycerin, and fatty acids. Lecithin is separated from soybean oil by the addition of water and centrifuging. It is purified prior to use as a food additive. Lecithin typically sells for about $0.50 per pound (CMR, 2003).

Solvents

To first remove the oil from the soybean, the beans must undergo some sort of extraction process. This can take place via either pressure extraction or solvent extraction. The extraction of oil by expeller, sometimes called a screw press, is a physical process. The oil is squeezed from the heated soybeans. However, most conventional processors in the U.S. use solvent extraction. In that process a solvent, usually hexane, is used to leach the oil from the soybeans. In pressure extraction the only products are oil, meal, and trace amounts of water. However, in solvent extraction, the extraction fluid must be separated from the raw oil. After a distillation step, the solvent can then be recycled in the system and used again.

Alcohol

Methanol is one of the two main reactants in the biodiesel process. As with any reaction, the efficiency is not 100% and not all of the alcohol will go to produce biodiesel and glycerol. This excess alcohol vapor can be recaptured and recycled back to the feed to be used again in the main process. Maintaining an efficient recycle stream can lead to reduced process costs by reducing the amount of methanol wasted in the process. By recycling, the excess alcohol is no longer a waste.

Acid or Base

During transesterification, an acid or base is used as a catalyst for the reaction. By definition, a catalyst is not used up in the reaction and therefore should be recycled. Such is the case in the biodiesel process. The acid or base can be reused after a separation step. Most large scale biodiesel operations use base catalyzed reactions due to their favorable economics (NBB, 2003). Low temperature, low pressure, and high conversion make the base catalyzed reaction far more feasible. The most common bases used are sodium and potassium hydroxide, and are usually mixed with the methanol before reaction.

Soap

When water builds up in the system, soap can form as a product. While soap can be sold as a commodity, it takes away from more profitable products. Because of this, the process should be set up in such a way that minimizes the production of water.

Water

Very little water is associated with this process. Minute amounts of water may be present in the soy beans before oil extraction, but this water should be dealt with before it enters the biodiesel process. Due to the water that can get into the process after pressing the beans, soap can form in the system. This soap combines with the glycerol and makes it difficult to separate. It is common for crude oil to be degummed prior to caustic refining (Weingartner, 2003). Usually oil refiners add acid to the soap stock to form an acid oil that can be sold to fatty acid processors. If the soap stock has not been degummed prior to caustic refining, then an acid oil water emulsion will form which will be a problem. Caustic refining of degummed oil in a self cleaning centrifuge will minimize the waste disposal problems (Weingartner, 2003). The only other water associated with the process is in the heating unit. Steam is used to heat the process, but it condenses in its own loop and is not a waste water issue. Additionally, management of the wash waters must be considered.

Other

Depending on the feed used, other various wastes and products may come about. Used cooking oil may have particulates that need separating. Beef tallow and other animal fats may have minerals as well as higher levels of free fatty acids and water which may interfere with the process. Used cooking oils and waste grease, while a cheap alternative to soybean oil as a feedstock, do not produce as much biodiesel and have various impurities that may become problematic as wastes (Patzer, 2002).

Chapter V: Characteristics of Biodiesel and Associated QA/QC

Biodiesel is covered under the standard ASTM D 6751-02. 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 United States Environmental Protection Agency as a fuel and as a fuel additive under Section 211(b) of the Clean Air Act (USEPA, 2003).

Physical/Chemical Characteristics of Biodiesel

The following list details some of the key characteristics of B100 biodiesel (Biodiesel Board, 2003; Canada Clean Fuels, 2003). Most of these are determined as acceptable characteristics under ASTM D 6751 specifications for biodiesel passed in 2002 (Majewski, 2002):

Specific Gravity	0.87 to 0.89 (slightly $>SG_{petro-diesel}$)
Composition	C12 - C22 FAME
Kinematic viscosity (40°C)	1.9 to 6 mm^2/sec
Cetane Number	>46 (typically from 40 to 70)
Heating value	16,928 to 17,996 btu/lb (~17,000 BTU/gal)
Sulfur content	<0.05% (v/v; typically 0.0 to 0.024%)
Cloud point	-11 to 16°C
Pour point	-15 to 13°C
Iodine number	60 to 135 g
Flash point	>130°C
Water and/or solids	<0.05% (v/v)
Ash	<0.02% (w/w)
Sulfur	<0.05% (w/w)
Oxygen	11% (by dif. w.%)
Copper strip corrosion	<No. 3
Carbon residue	<0.05% (w/w)
Acid number	0.8 mg KOH/g
Free glycerin	<0.02% (w/w)
Total glycerin	<0.24% (w/w)
Phosphate content	<0.001% (w/w)

ASTM D 6217 can be used to measure the quantity of insoluble fuel contaminants. ASTM D 6751-02 is composed of several standards, and biodiesel must meet each of these standards before it can be considered suitable as a fuel. To clarify which of the above listed

characteristics are formally part of the list comprising ASTM D 6751-02, Table V-1 lists the official standards that do comprise ASTM D 6751-02.

Storage Tank Testing

Storage tanks for biodiesel should be kept free of water, and provisions for draining water out of the tanks on a regular basis should be made. Water may seep into storage tanks during rains, and water that is not separated from the biodiesel during processing could also form a layer during storage. Underground or isothermal storage tanks are recommended, but if the storage tanks are above ground, then the tanks should be sheltered or painted with reflective paint. This is due to the fact that high temperatures can increase fuel degradation. The level of exposure to oxygen by the tanks should also be limited. This will increase the product life of the biodiesel. If biodiesel has been in storage for a long time, it may be wise to replace the aged fuel with a fresh supply. The need for replacing aged biodiesel is determined by testing, and ASTM D 6751-02 advises that a plan for monitoring the quality of bulk fuel be put into place. Biodiesel should be sampled under the standard ASTM D 4057, which provides guidelines for fuel sampling.

Flash Point

The flash point of biodiesel is determined by ASTM D 93. This method requires the use of a Pensky-Martens closed-cup tester of fuel oils (ASTM, 1994a). The flash point of biodiesel should be at least 130.0 $^{\circ}$C, and in general, biodiesel's flash point is higher than that of conventional #2 diesel. ASTM D 93 uses the flash point to describe the response of a material to heat. Therefore, the higher a material's flash point, the safer that material should be under heated conditions. Conventional #2 diesel should have a flash point of at least 52°C and typically the value is about 83°C (Williams Alaska Petroleum, 2003). Since biodiesel has a higher flash point than conventional #2 diesel, it is a safer fuel than conventional diesel.

Water and Sediment

ASTM D 2709 is the standard test method for determining water and sediment in fuels. At the most, biodiesel should contain only 0.050% by volume water and sediment. Large amounts of water and sediment in a fuel such as biodiesel tend to cause fouling of the fuel-handling facilities and also cause trouble in the fuel system of an engine (ASTM, 1994b). According to this standard, an accumulation of sediment in storage tanks and filter screens can obstruct the flow of oil from the tank to the combustor. Additionally, separating water from biodiesel before storage is essential. Water can lead to corrosion of storage tanks and equipment. As mentioned in the processing section of this report, water can be formed in the process of making biodiesel or introduced into the process through washing.

Viscosity

Viscosity is an important property of any fuel as it is an indication of the ability of a material to flow. In an engine, it is desirable to have a fuel that flows well, and a lower viscosity is indicative of good flow. According to ASTM D 445, dynamic viscosity of a fluid can be found from the density and kinematic viscosity (ASTM, 1994c). This standard actually provides the method for obtaining the kinematic viscosity and the calculation method to determine the dynamic viscosity. However, ASTM D 6751-02 only requires a measurement of the kinematic viscosity. For biodiesel, the kinematic viscosity at 40°C should be between 1.9-6.0 mm^2/s. It is important to note that viscosity is determined at a specific temperature. This is due to the fact that, for liquids, viscosity is dependent upon temperature. For a liquid, kinematic viscosity varies with temperature over a narrower range than dynamic viscosity. For conventional diesel, the viscosity is typically 3.6 mm^2/s; however, biodiesel usually has a higher viscosity than conventional diesel (Majeeski, 2003; Williams Alaska Petroleum Inc., 2003).

Sulfated Ash

ASTM D 874 is the standard test method for determining sulfated ash from lubricating oils and additives. ASTM D 874 describes the methodology to determine the sulfated ash from unused lubricating oils containing additives and from additive concentrates used in compounding (ASTM, 1994d). The additive concentrates usually contain at least one of the following metals: barium, calcium, magnesium, zinc, potassium, sodium, and tin as well as other elements such as sulfur, phosphorous, and chlorine. Biodiesel additive concentrates come from catalysts. Alkali catalysts such as sodium hydroxide and potassium hydroxide are used to conduct base-catalyzed transesterification. In case of feedstocks with high free fatty acid content, the catalyst is sulfuric acid. Catalysts used in base or acid catalysis are almost completely removed from biodiesel during the washing steps. Unremoved traces can contribute to problems with injectors, fuel pumps, pistons, and ring wear, along with the formation of engine deposits (ASTM, 2003a). ASTM D 874 requires that a sample of biodiesel be carbonized, the remaining residue be treated with sulfuric acid, and be heated to constant weight. The maximum sulfated ash level allowed is 0.20% by weight.

Total Sulfur Content

The amount of total sulfur in motor fuels is determined by ASTM D 5453. This standard uses ultraviolet fluorescence to detect trace amounts of sulfur in fuels (ASTM, 1994e). For biodiesel, the allowable sulfur content has an upper limit of 0.05% by weight. For conventional #2 diesel, the sulfur content has an upper limit of 0.50% by weight (Williams Alaska Petroleum Inc., 2003). Since the limit on sulfur is 10 times smaller for biodiesel, the amount of pollution derived from sulfur after a fuel has been burned is greatly reduced. This leads to less emissions

Corrosion

ASTM D 130 is used to measure the level of copper corrosion that would occur if biodiesel were used in any application where metals such as copper are present. The test is accomplished by using a copper strip tarnish test. A polished copper strip is immersed in a sample of biodiesel and heated for a specified length of time at a specified temperature. The copper strip is removed, washed, and is then compared to the ASTM certified Corrosion Standards (ASTM, 1994f). The maximum corrosion allowed is that corresponding to a No. 3 Copper Strip Corrosion Standard.

Cetane Number

The cetane number of biodiesel is determined by ASTM D 613. The cetane number can be defined as a measurement of the ignition performance of a diesel fuel oil obtained by comparing it to reference fuels in a standardized engine test (ASTM, 1994g). The cetane number for biodiesel should be a minimum of 47; however, as discussed before, a cetane number that is too high can lead to engine problems. Biodiesel cetane number depends on the feedstock used for its production. Table V-2 lists cetane numbers for biodiesel derived from some common feedstocks. The esters presented in Table V-2 are methyl esters. If an alcohol other than methanol is used during transesterification, the resulting esters will have a different cetane number.

Cloud Point

Another important property of biodiesel is its cloud point, which is determined by ASTM D 2500. The cloud point is defined as the temperature at which a cloud of wax crystals first appears in a liquid when it is cooled under the conditions prescribed in ASTM D 2500 (ASTM, 1994h). Typically, as the cetane number increases, the cloud point increases as well. Therefore, the cloud point depends upon the feedstock used and must be taken into consideration if the fuel is to be used in cold environments.

Carbon Residuals

ASTM D 4530 is the standard test method for determination of carbon residue. In fuels, carbon residue is the part remaining after a sample has been subjected to thermal decomposition

(ASTM, 1994i). This test provides some indication of the coking tendencies of a fuel such as biodiesel. It is performed via heating a weighed sample of biodiesel to 500°C under a nitrogen atmosphere for a specified length of time. While at these conditions, the sample experiences coking reactions and any volatiles that are formed are purged by the nitrogen. The residue that remains is the carbon residue. The maximum limit for carbon residue in biodiesel is 0.050% by mass.

Acid Number

The acid number of biodiesel can be found using ASTM D 664. The acid number is a measure of the amount of acidic substances in a fuel under the conditions specified by this standard. The acid number can provide an indication of the level of lubricant degradation while the fuel is in service (ASTM, 1994j). For biodiesel, the standard calls for a maximum acid number of 0.80mg KOH/g. The acid number is directly related to the free fatty acid content discussed before. The higher the free fatty acid content, the higher the acid number. The acid number can become a serious issue when feedstocks with high free fatty acids are used to produce biodiesel.

Total and Free Glycerol Content

ASTM D 6584 is used to measure free glycerol and total glycerol in biodiesel. One of the products of the transesterification reaction is glycerol (or glycerine). A small concentration of glycerol remains in the biodiesel after the first separation step. Washing the biodiesel can reduce this amount, but the washing process is not 100% efficient and some glycerol will still remain in biodiesel. Glycerol can be free or bonded. Free glycerol is the amount of glycerol not in glyceride bonds, and bonded glycerol is the amount of glycerol in mono-, di-, and triglyceride bonds. Total glycerol is the sum of free and bonded glycerol. A high amount of free glycerol can cause problems during storage or in the fuel system due to the separation of the glycerol. The free glycerol content of biodiesel should not exceed 0.020% by mass. A high total glycerol level can result in injector fouling and may also contribute to the formation of deposits at injection nozzles, pistons, and valves (ASTM, 1994k). For biodiesel, the maximum amount of total glycerol should be 0.240% by mass. The amounts of total and free glycerol are determined using gas chromatography.   First, the biodiesel sample is silyated with N–methyl—trimethylsilyltrifluoracetamide (MSTFA).   Then the sample is analyzed with gas chromatography. Mono-, di-, and triglycerides are determined by comparing the output peaks to monoolein, diolein, and triolein standards, respectively. Average conversion factors are used to calculate the bonded glycerol content.

Phosphorous Content

Some fuel additives may contain phosphorous, which can damage catalytic converters used in emissions control systems (ASTM, 2003a). The level of phosphorous in biodiesel is measured using ASTM D 4951. For biodiesel, the amount of phosphorous must be kept below 0.001% by mass. This standard uses Inductively Coupled Plasma Atomic Emission Spectrometry to measure the phosphorous content (ASTM, 1994L). A biodiesel sample is weighed and diluted with mixed xylenes or other suitable solvent on a weight-by-weight basis. Standards are prepared using a similar procedure. A peristaltic pump introduces the solutions to an inductively coupled plasma atomic emission spectrometer, and phosphorous content is determined by comparing standard and sample atomic emission intensities at wavelengths associated with phosphorous.

Boiling Point

Another important property of any material is its boiling point. ASTM D 1160 is the standard test method for distillation of petroleum products at reduced pressures. This method determines the range of distillation, including the initial boiling point, the final boiling point, and a distillation curve relating volume percent distilled and atmospheric equivalent boiling point temperature (ASTM, 1994m). However, according to ASTM D 6751, biodiesel exhibits a boiling point and not a distillation curve, and the boiling point should be below $360^{\circ}C$.

Table V-1. Biodiesel Requirements (ASTM, 2003a)

Property	Test Method	Limits	Units
Flash Point (Closed Cup)	D 93	130.0 minimum	^{o}C
Water and Sediment	D 2709	0.050 maximum	% volume
Kinematic Viscosity, 40°C	D 445	1.9-6.0	mm^2/s
Sulfated Ash	D 874	0.020 maximum	% mass
Sulfur	D 5453	0.05 maximum	% mass
Copper Strip Corrosion	D 130	No. 3 maximum	
Cetane Number	D 613	47 minimum	
Cloud Point	D 2500	Report*	^{o}C
Carbon Residue	D 4530	0.050 maximum	% mass
Acid Number	D 664	0.80 maximum	mg KOH/g
Free Glycerine	D 6584	0.020	% mass
Total Glycerine	D 6584	0.240	% mass
Phosphorous Content	D 4951	0.001 maximum	% mass
Distillation Temperature, Atmospheric Equivalent Temperature, 90% recovered	D 1160	360 maximum	^{o}C

* Biodiesel's cloud point is usually higher than conventional diesel, and this fact should be taken into consideration when blending.

**Table V-2. Cetane Numbers of Biodiesel Derived from
Different Feedstocks (Majewski, 2003)**

Feedstock	Cetane Number of Biodiesel
Cottonseed	51.2
Rapeseed	54.4
Safflower	49.8
Soybean	46.2
Sunflower	46.6

Chapter VI: Overview of the Economics Associated With the Biodiesel Industry

Diesel Use Within the United States and Mississippi

The diesel industry represents over $50 billion per year of economic activity within the United States. The US DOE (IA State, 2003) estimates that the total United States annual diesel usage in 2000 was 33 billion gallons. Frazier (2002) reports slightly higher figures for diesel use within the United States during 2000 was over 55 billion. The Mississippi Department of Agriculture and Commerce (2003) reports that the total diesel consumption within Mississippi during 2001 was 505,679,000 gallons. It is also reported that Mississippi ranked 26th among the states in terms of diesel usage. Another interesting statistic is that diesel fuel usage within the United States appears relatively constant over the past several years.

Frazier (2002) presented interesting data concerning the use of petroleum and biodiesel within both the United States and Mississippi. These data show that the primary users of diesel within the United States (in descending order) are the trucking industry (over 30 billion gallons per year), residential (over 3 billion gallons per year), agriculture (over 3 billion gallons per year), railroad (approximately 3 billion gallons per year), and industrial operations (over 2 billion gallons per year). Mississippi had slightly different trends. The trucking industry was the largest user in Mississippi at over 0.5 million gallons per year. The next largest user was agriculture at 0.08 million gallons per year, followed by industrial operations at 0.03 million gallons per year. Rail was another significant user of diesel fuel in Mississippi at approximately 0.02 million gallons per year. Frazier also presents potential biodiesel usage within United States and Mississippi using B2 and B20 as the two options for establishing a biodiesel market. He calculates an annual total biodiesel usage of over 14 million and 0.14 million within the United States and Mississippi, respectively. Clearly, if costs can be reduced, a favorable market can be established for biodiesel. Additionally, distribution infrastructure development will not be an issue for biodiesel, since much of the petroleum diesel infrastructure will easily support the inclusion of biodiesel into the market.

Diesel and Biodiesel Prices

Petroleum diesel prices over the past several years have generally ranged from about $0.50 to $1.40 per gallon (Coltrain, 2002). The consumer price of biodiesel within most areas of the United States generally lies within the $1.50 - $3 per gallon range (Donovan et al. 1998; Prakash, 1998; Coltrain, 2002; MDAC 2003; University of Idaha, 2003; US DOE, 2003). Approximately 80% of this price is attributed to plant oil costs (Coltrain, 2002). Majewski (2002) reports that biodiesel consumer prices at the pump are 2 - 3 times that of petroleum diesel. B5 blends are reported by Coltrain (2002) to be only $0.05 to $0.10 per gallon more than neat petroleum diesel.

There are some savings that may be realized via the economy of production scale. Environment Canada (2003) reports that increasing the size of the production output can potentially reduce production costs by as much as 30%. No definition of "size scaling" was provided, but the concept of economy of scale is well known among the chemical production industry. To further highlight this point, researchers from the University of Arkansas state report that a 3 million gallon per year biodiesel facility will cost $2 to $3 per gallon of annual production (Bennett 2002). They also state that a 30 million gallon per year facility would cost as little as $0.50 per gallon of annual production. The net result in terms of savings on a per gallon of biodiesel produced equates to a $0.40 per gallon savings (assuming a constant feedstock cost, with no mention of glycerol market considerations made). The Department of Energy reports that large scale operations producing biodiesel will probably be able to produce the fuel at about $1.50-$1.60 per gallon with no real definition of scale for this estimate provided; however, it is very likely that these figures are derived for system production capacities well over 10 million gallons per year (PPRC, 1999).

Another aspect concerning the economics associated with adopting biodiesel is the total cost to state entities considering utilizing biodiesel and/or B-blends within their fleets. If only the direct cost to purchase the bulk fuel is considered, obviously an increase in operational cost will be estimated. However, when considering the taxes generated from the siting of a biodiesel facility within the state, the potential exists that the total cost to the state may be minimal, or possibly, none at all. SeQuential Fuels Inc. (Eugene, OR) reports that an Iowa study found that the if the State of Iowa converted their entire diesel fleet to a B20 blend and a 5 million gallon per year production facility was sited in the state, that the state will actually realize a net profit on such a venture.

In terms of feedstock costs, soy oil and most other plant oil typically run within the low $0.20 per pound range (Chemical Market Reporter, 2002). Yellow grease is reported to cost approximately half this price which substantiates the recent high level of interest in animal-based feedstocks (Chemical Market Reporter, 2002). In fact, brown grease has been reported to be available in some regions at cost levels within the $0.03 per pound range (Canakei and Van Gerpen, 2001). Utilizing the cheaper animal-based feedstock and acknowledging that the final product may not have great cold flow properties, there appears a high potential to reduce biodiesel market prices to those approaching that of petroleum diesel.

Rice et al. (1997) evaluated the economic benefits of producing biodiesel in Ireland by comparing production cost between rapeseed and tallow. They conclude that a 15% reduction in production cost would be realized using tallow instead of rapeseed under the agricultural and industrial conditions within Ireland.

Recent work by the US DOE to establish mustard seeds as a biodiesel feedstock indicate that the cost of this new oil would be approximately $0.10 per pound (about half of soy oil). This would place the cost of the final biodiesel product in the $1 per gallon range (Coltrain, 2002).

The University of Missouri-Columbia presents compelling information concerning the feasibility of establishing a community-sized biodiesel facility (Weber et al., 2003). This scenario involves total community involvement from soybean growing to localized product utilization. Their model evaluated a 0.5 million gallon per year production facility. They

estimate that the cost of producing biodiesel under these conditions would fall within the mid-$1.20 per gallon range.

Other Production Costs

While feedstock costs are clearly the dominant cost associated with biodiesel production, other costs must be taken into account. Coltrain (2002) states that one study estimated transesterification costs to be approximately $0.50 per gallon of produced biodiesel. Overhead cost were reported to be in the $0.30 per produced gallon range. Transportation costs were estimated for regional markets to be $0.07 per gallon.

Production Plant Construction Costs

Evaluation of data reported by CAS Inc. (2002) indicates that the cost of constructing a rapeseed biodiesel production facility in Canada is approximately $1 per gallon of production capacity. The Chemical Market Reporter (2002) states that a new facility in North Carolina will cost $3.75 per gallon of annual production. Discussions with Lurgi PSI, Memphis, TN, indicate that $1 - $1.50 per gallon of annual production is a good estimation for planning purposes (Personal Communication between Lurgi Officials and Dr. Mark Zappi, 2003). Millennium Fuels Corp. (2003) reports that the capital cost for a 5 million per year biodiesel production facility (batch) typically costs $1 to $1.30 per gallon of annual capacity; however, they claim that a new continuous flow plant has cheaper capital costs at $0.70 per gallon of annual capacity.

Other Key Economic Factors

As stated in the Introduction Section of this report, glycerol often dictates the profitability of a biodiesel plant. Identifying and maintaining this market is absolutely critical to a successful biodiesel venture. A potential glut in the glycerol market is of concern to the further development of the biodiesel industry (Personal communication with West Central Soy personnel, 2002). Current uses for glycerol are many including pharmaceuticals, cosmetics, paints, and toothpaste.

When taking into account the total plant crop, Coltrain (2002) reports that the meal generally constitutes the largest profit margin for the processors (approximately 60% for soy). Clearly, some integration of investment opportunities exist for the grain processors to be involved in both the meal and oil markets. Frazier (2002) estimated, during a feasibility study of a integrated soybean processing/biodiesel production facility in either Michigan or Ohio, that one bushel of soybeans would yield 1.44 gallons of biodiesel, 44 lbs. of high protein soybean meal, 3.6 lbs. of hulls, and 1.33 lbs. of glycerol.

Chapter VII: Handling of Biodiesel

The intent of this chapter is to present a summary of issues concerning the handling of biodiesel products. Note that Dr. Shane Tyson of the DOE National Renewable Energy Laboratory in Golden, CO (Tyson, 2001) presents much more detail on mixing and storage issues in her document entitled <u>Biodiesel Handling and Use Guidelines</u> (DOE document NREL/TP-580-30004). The reader is referred to her document for more information concerning handling and cold weather issues. Neat biodiesel requires handling procedures similar to those utilized with vegetable oils. However, appropriate care should be taken when handling petroleum/biodiesel blends due to issues related to the petroleum fraction.

Biodiesel should be stored in tanks made of compatible materials that include steel, aluminum, fluorinated polyethylene, fluorinated polypropylene, and Teflon (SeQuential Fuels, 2003). Materials that should be avoided include copper, brass, lead, tin, and zinc. As mentioned above, care should be taken to ensure that biodiesel does not contact rubber products, including hoses, gaskets, and seals. Biodiesel is described by Tyson (2001) as a mild solvent; therefore, prolonged contact of biodiesel on painted and varnished finishes should be avoided. As noted in the performance experience discussions from this document, biodiesel tends to act as a cleansing agent; therefore, adding biodiesel to tanks that has attached solids may result in the detachment of the solid into the bulk fluid potentially causing plugging problems during fuel pumping.

When storing neat biodiesel at temperatures lower than 45°F, problems with "gelling" may be encountered. Biodiesel should be stored underground in most cold climates. However, if above-ground storage is used then blending with anti-gel agents or with No. 1 or No. 2 diesel fuel can be used to control gel problems, along with the use of tank heaters and/or insulation. Tyson (2001) recommends that biodiesel fuels should be stored at temperatures at least 15°F above their pour point, which is feedstock dependent characteristic (30°F to 56°F).

If stored or mixed biodiesel form crystals due to temperatures being too low, then Tyson (2001) suggests the following to remove the crystals:

a. Allow ambient atmospheric conditions to warm the solution
b. Force heat the fuel to above 100°F or until the crystals disappear
c. Filter our the crystals, but keep them for reuse when they melt

Storage stability of biodiesel is a key issue to the industry. Oxidative degradation can result in the formation of solids and gums within the fuel (Tyson, 2001). The tendency to be unstable can be predicted via the number of unsaturated carbon-carbon bonds within the feedstock triglycerides. Fuels containing a high number of double bonded oil and/or fats tend to oxidize more rapidly than saturated feeds. Tyson (2001) states that instability increases by a factor of 1 for every unsaturated bond present on the fatty acid chain; therefore, the fatty acid C18:3 (where, CX:Y with X = number carbon atoms and Y = number of double C:C bonds), being three times more unstable than a C18). The stability test described in ASTM D 2274 can

be used to assess stability characteristics of a biodiesel. Stabilizers can be added to eliminate stability problems. Biodiesel or BXX blends should not be stored beyond 6 months, until more data are made available (Tyson, 2001; Clean Air Fleets, 2003). Obviously, this has great implications to processing plant production scheduling and distribution planning.

Biological activity within biodiesel can also pose stability problems, mostly associated with slime and solids formation. Tyson (2001) recommends that biocides be considered within systems where biogrowth problems have been observed. Often the bioactivity is associated with water supporting algae growth; therefore, improved housekeeping operations can be used to control algal growth (Tyson, 2001).

Chapter VIII: Environmental Implications of Biodiesel Use

     Biodiesel does not contain chemically hazardous materials (Tyson, 2001). However, it does contain chemicals that do impart an oxygen loading on receiving environments. Therefore, long-term leakage or large spills into the environment can cause adverse impacts due to excessive oxygen utilization causing anaerobic (septic) conditions to become established. Environmental release of biodiesel is considered much less of an environmental security issue than the release of petroleum diesel because of the ease of biodegradation associated with the biodiesel (Peterson et al., 2002). Additionally, biodiesel is not considered a toxic compound due to its oil-base (i.e. not petroleum).

     The US Biodiesel Board (2003) reports that studies show that the use of biodiesel reduces exotic (derived from outside of the biosphere) carbon dioxide flux into the biosphere by over 75% because of recycling of the carbon dioxide within the biosphere. Carbon monoxide production on a life cycle basis is reduced by approximately 35%. Measurements of particulate matter emissions from diesel-run buses indicate a reduction of particulates by over 60%. Soot (the black smoke released during rpm increases) within the same tests were reduced by over 80%. Sulfur dioxide and methane releases have been documented to be reduced by over 8% and 3%, respectively. Nitrogen oxide releases were approximately 9% higher than those measured from combustion of petroleum diesel fuel. Wastewater production and hazardous waste generation during processing of biodiesel over petroleum diesel is approximately 80% and 95%, respectively, lower.

     Sharp (1998) reports similar emission numbers for the burning of neat biodiesel within a Cummins N14 diesel engine. He estimate reductions in hydrocarbons, carbon monoxide, and particulates in excess of 95%, 45%, and 30%, respectively. However, he also measured a 13% increase in nitrogen emissions. Additionally, his results included data to show a 90% decrease in polycyclic hydrocarbon release.

     Since biodiesel contains no aromatic compounds, it is far more environmentally friendly than petroleum derived diesel which does contain many aromatic compounds (Majewski, 2002). The lack of aromatic compounds within biodiesel reduces the extent of polycyclic aromatic compounds formation during combustion within diesel engines. Tyson (2001) reports that biodiesel degrades within the environment approximately four times faster than petroleum diesel.

     In terms of long-term human health benefits, Canada Clean Fuels (2003) reported that the use of B100 would reduce cancer cases due to diesel combustion by over 90%. They also state that using B20 would reduce this risk by approximately 25%.

     Note with regard to direct human handling issues, biodiesel appears to be relatively passive outside of reported skin and eye irritation when directly contacted. Ignition is a safety issue that should be evaluated as part of a site safety assessment; biodiesel is a fuel. The reader is strongly suggested to access the Material Data and Safety Sheet (MSDS) for biodiesel available from suppliers or from the world-wide web. The MSDS presents information on handling safety, first aid, and fire fighting procedures among other useful information. Note that government regulations require MSDS sheets for all chemicals used within industrial operations be on hand for employee and community member review.

Chapter IX: Oil Yields from Selected Agricultural Crops

This chapter is provided to give interested parties some insight into the amount of oil that can be produced from various agricultural crops. This information was collected from the Journey to Forever Website (Journey to Forever, 2003).

Crop	Kg oil/ha	Liter/ha	Lbs/ac	Gal/ac
Corn	145	172	129	18
Kenaf	230	273	205	29
Hemp	305	363	272	39
Soybean	375	446	335	48
Linseed	402	478	359	51
Mustard seed	481	572	430	61
Camelina	490	583	438	62
Sesame	585	696	522	74
Safflower	655	779	585	83
Rice	696	828	622	88
Tung Oil	790	940	705	100
Sunflower	800	952	714	102
Peanuts	890	1059	795	113
Rapeseed	1000	1190	893	127
Castor	1188	1413	1061	151
Pecan	1505	1791	1344	191
Palm	5000	5950	4465	635

Note that when evaluating the yields of these products, the chemical composition of the oil, climate compatibility in terms of culturing these crops within the geographic area of interest, ease of oil extraction, cultivation/processing costs, general oil markets, and potential meal uses must be taken into account. All of these of factors will dictate resulting oil costs and the stability of the feedstock resources required to sustain steady production of biodiesel to meet market commitments.

Chapter X: Compilation of Biodiesel Facility Design Firms

The following list developed by the author team presents a compilation of design firms claiming to have expertise/experience with the design of biodiesel plants. Note that this list was taken from the database of the authors. The list is likely not a complete list, nor does the presence of a particular company infer any certification or acknowledgement of performance. It simply represents information concerning those groups found to date claiming to have expertise with plant construction and/or to be equipment vendors.

Company	Location	Phone Number
BDT Biodiesel Technologies (Division of CHL Handels-und Projektierungs GmbH)	Vienna, AUSTRIA	43-1-877-0553
Biodiesel Gear	Collinsville, IL	618-344-8853
Biodiesel Industries	Las Vegas, NV	877-246-3835
BIOX Corp.	Toronto, ONTARIO CANADA	905-337-3972
Bioresource Fuels, LLC (Resodyn Corp.)	Butte, MT	406-723-2222
Bratney Companies	Des Moines, IA	800-247-8755
Crown Iron Works	Roseville, MN	651-639-8900
Ekoil Biodiesel Production	Bratislava, SLOVAKIA	421-7-4820-8811
Energea	Vienna, AUSTRIA	43-1-729-9401
Frazier, Barnes, and Associates	Memphis, TN	901-725-7258
European Biofuels Group	Hampshire, UNITED KINGDOM	44-1730-829238
Griffin Industries	Cold Spring, KY	859-572-2558
Lurgi PSI Inc.	Memphis, TN	901-756-8250

North American Biorefinery Resources	Sr. Louis, MO	314-664-1900
Pacific Biodiesel	Kahului, HI	808-871-6624
Savoia (Abatec, s.a.)	Bella Vista, ARGENTINA	5411-4754-4796
Stratco Inc.	Scottsdale, AR	480-991-0450
Superior Process Technologies	Saint Paul, MN	612-924-7184
Renewable Products Development Laboratories Inc.	Lincoln, NE	402-465-8883
Westfalia Separator Inc.	Northvale, NJ	800-722-6622
World Energy Alternatives, LLC	Chelsea, MA	617-889-7300
Yokayo Biofuels	Ukiah, CA	877-806-0900

Chapter XI. Compilation of US Biodiesel Producers

The following is a listed compilation of known biodiesel producers identified to date.

Company	Location
Biodiesel Industries	Las Vegas, NV
Imperial Western Products	Coachella, CA
Stepan Company	Millsdale, IL
Blue Sun	Ft. Collins, CO
Ag Processing	Omaha, NE
American Biofuels	Bonita, CA
Columbus Foods Company	Chicago, IL
Filter Specialty	Autryville, NC
Imperial Western	Indio, CA
Interwest, LC	Ralston, IA
Pacific Northwest Biodiesel LC.	Aloha, OR
Peter Cramer North America LP	Cincinnati, OH
Southern States Power Company	Ontario, CA
Stephan Company	Northfield, IL
Sustainable Systems, LLC	Missoula, MT
World Energy Alternatives LLC	Chelsea, MA
NOPEC Corp.	Lakeland, FL
West Central Soy	Ralston, IA

Griffin Industries	Cold Spring, KY
Ocean Air Environmental	Lakeland, FL
AGP	Sergeant Bluff, IA
Pacific Biodiesel	Kahului, HI
Iowa Lakes Processing	Millford, IA
World Energy Alternatives	Cincinnati, OH
Twin Rivers Technology, LP	Quincy, MA
Corsicana Technologies	Corsicana, TX

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ASTM, 1994e, "D 5453-93: Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels and Oils by Ultraviolet Fluorescence," West Conshohocken, PA.: ASTM.

ASTM, 1994f, "D 130-88: Standard Test Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test," West Conshohocken, Pa.: ASTM.

ASTM, 1994g, "D 613-93: Standard Test Method for Cetane Number of Diesel Fuel Oil," West Conshohocken, Pa.: ASTM.

ASTM, 1994h, "D 2500-91: Standard Test Method for Cloud Point of Petroleum Products," West Conshohocken, Pa.: ASTM.

ASTM, 1994i, "D 4530-93: Standard Test Method for the Determination of Carbon Residue (Micro Method)," West Conshohocken, Pa.: ASTM.

ASTM, 1994j, "D 664-89: Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration," West Conshohocken, Pa.: ASTM.

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