Today's Lipid to Renewable Diesel Fuel Market

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Abstract

For almost a full decade, the bio-based vehicular fuels industry has been anticipating the establishment of a continually expanding industry within a reasonably stable market base. However, a variety of events in the bio-based diesel fuel industry has resulted in this promising market still remaining dynamic. Of the five renewable, bio-based fuels that appear to have potential to displacement petroleum diesel within the United States and elsewhere, biodiesel and green diesel are believed to be the fuels that in the near-term represent the most promising options. Even though they are both viable displacement options and blend well with petroleum-based diesel these fuels are chemically different, created using completely different processing systems. While both are considered promising, biodiesel is fully commercialized with green diesel generally considered to be at the demonstration stage. Upon review of how the two fuels are produced and potentially marketed, there does exist the potential for both feedstock and market competition to develop between biodiesel and renewable diesel.

Keywords: *Renewable Energy, Biodiesel, Green Diesel, Lipids, Fuels Processing*

1. Introduction

The realization of the finiteness of fossil fuels and their potential for adverse ecological impact has prompted a global initiative to find new sources of vehicular fuels which are produced from renewable feedstocks, while greatly reducing ecological threats. Additionally, from the perspective of the United States, developing sources of vehicular fuels that are derived from domestic feedstocks are of key strategic interest [1]. Unfortunately, currently well over 50% of the petroleum used within the United States is derived from foreign reserves. The cost and politics of being totally dependent on these reserves is getting progressively more expensive from both a strategic and sociological standpoint. Clearly, a renewable source of diesel fuel is badly needed for meeting the future energy needs of the United States.

Society produces a wide variety of biomass-based carbon reservoirs via farming and/or waste generation that can be harnessed to meet its power requirements in the form of gaseous, liquid, and solid fuels. Of these, liquid fuels are considered of higher importance. Fuels produced from biomass have been for some time generally considered one of the most promising alternatives to the use of petroleum as a source of liquid fuels. Hence, over the past ten years, a significant developmental effort has resulted in the development of several bio-based diesel options that do perform well within most vehicles used today. These fuels generally have low toxicity, are easily biodegraded within the environment if released, and produce much fewer air-borne pollutants in internal combustion engines than petroleum fuels [2-4].

2. Renewable Diesel Fuels

Renewable fuel options for displacing petroleum-based diesel fuel in the United States may be categorized based on the feedstocks used for producing them. The first category is "Lipid Only Based" fuels (LO fuels) which use only use lipids (fats, oils, or greases, aka. FOG) as the key feedstock component for their production. The other category is "Broad Feedstock Based" fuels (BF fuels) which can use a wide variety of sources as the primary production component of their formulation. The most viable and developed fuels categorized as LO Fuels are biodiesel, green diesel, and straight vegetable oil (SVO). Biodiesel and green diesel are the focus of this paper because they represent by far the most developed fuels from a petro-diesel displacement perspective.

Technically, SVOs can be directly used within diesel engines; however, they have several characteristics that do not support widespread usage. This is primarily due to their high viscosity under most operating conditions and poor cloud point number causing gelling during cold 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 use petroleum fuels [5]. Vegetable oils have less than desirable characteristics when used directly as a fuel and not transformed into alcohol esters [6]. Conversion of the vegetable oil into a better fuel product has been undergoing development and optimization over the past several years. Therefore, it was decided to not feature SVO in this paper. It represents a non-processed fuel which most experts agree will result in long-term adverse engine impacts. However, the authors do note that there is a growing movement underway to modify diesel engines to better utilize SVOs with minimal damage. These modifications also address several oil characteristics which pose problems from both delivery and operations standpoints in terms of effectively injecting neat SVO into the engine combustion chamber.

Fuels which fit under the category of BF Fuels include thermal depolymerization and gas to liquid fuels. Both of these fuels utilize thermal processing as a key step in their production. With thermal depolymerization (TDP) fuels, thermal energy is used to depolymerize the feedstocks into volatilize organic compounds. The process is applicable to any organically-based feedstocks. The volatilized organic compounds are separated and returned to liquid form via a separatory condenser. Examples of TDP fuel feedstocks which may be used include waste meat products, tires, plastics, waste oils, and demolition wastes. In the case of gas to liquid or GTL fuels, the feedstock is gasified within a gasifier to produce synthesis gas. This is then processed via a reactive catalytic processing step (Fischer Tropsch catalyst) to produce a liquid stream which is separated into various components via distillation. The diesel cut is used as the GTL diesel fuel. The GTL process may also be used to produce a gasoline displacement fuel via the use of a different catalyst. Potential feedstocks for GTL fuels include coal, cellulosic materials, tires, and demolition wastes, making this technology literally the most flexible of all of the processes discussed from a feedstock usage standpoint.

It is interesting to note that lipids can also serve as a feedstock for BF Fuels production; however, this would be a costly option for these processes. The ability to use cheaper feedstocks is one of the biggest advantages for BF Fuels. Conversely, both TDP and GTL fuels are both more costly to produce than biodiesel and green diesel due to costs associated with thermal conversion and downstream processing. Additionally, neither are being produced at a large commercial scale; however, this may change over time and, in fact, these fuels may become a fuel of choice as they are further developed. In particular, the potential for GTL is considered very high in the viewpoint of the authors. With time, this process may end up being a major fuel within the United States given the available of domestic sources of low-grade coal and lignocellulosic materials which can serve as cheap feedstocks.

3. Lipids of Fuel Production Value

The lipids used with both biodiesel and green diesel production are actually only part of the lipid class of chemicals. In the case of biodiesel and green diesel, the current lipids of choice primarily come from plants and animals [6-9]. Albeit, a significant effort is underway to discover economical non-traditional microbial sources of these lipids [9, 10]. Other sources include non-standard animals such as alligators [11]. Since these lipids represent the bulk of the compositional aspect for biodiesel and green diesel, a discussion concerning their makeup and cost is presented in this section. Chemicals classified as lipids include fats and oils, waxes, phosphoglycerides, sphingolipids, glycolipids, steroids, terpenes, prostaglandins, and fat-soluble vitamins [7]. In the case of the two fuels featured in this paper, free fatty acids and glycerides are of the most interest because they are the feedstocks used during production of both fuels. Fatty acids represent one of the two key components of glycerides which are common organic chemicals made up of a glycerin backbone with one, two, or three fatty acids. These are attached to the backbone carbons with are then referred to as monoglyceride, diglyceride, or triglyceride, respectively. Fatty acids are commonly identified by the number of carbons within the molecule and the number of unsaturated bonds present [8]. Hence, the fatty acid known as myristic acid is a "C14:0" or "C14" acid because it is composed of 14 carbons and no unsaturated bonds. Oleic acid is a "C18:1" fatty acid because it has 18 carbons and one unsaturated bond. Other examples include lauric acid (C12:0), palmitic acid (C16:0), palmitoleic acid (C16:1), and linoleic acid (C18:2).

Table 1: Oil Production Capacity by Feedstock

Feedstock	Production [gallons/acre]
Soy	55
Sunflowers	100
Rapeseed	150
Jatropha	200
Palm	650
Chinese Tallow	850
Algae	[a]>1000

[a)]Between 3,000 and 10,000 gallons are often quoted

Example lipid sources of industrial value which also represent a potential to be key feedstocks within the United States can be seen in Table 1, using a gallon of oil per acre production perspective listing [12-14].

It is interesting to note from the data listed by Durret that palm and soy oils dominate the current global lipid market. Both are produced at an approximate rate of 35 MMT per annum [6]. However, when comparing these two highly produced lipid sources to each other, the difference is dramatic from per acres yield perspective in that palm has one of the highest per acre yields compared to soy with the lowest. As biofuel markets mature, the potential exists that soy oil will eventually lose its market-share to the other feedstock sources with much higher yields. One key point to note is that as the more novel lipid feedstocks are developed, then the utilization of resulting meal must be addressed or these options may not be economically viable.

As discussed above, the fatty acids attached to the glycerin background are very often critical in terms of lipid's value to an industry [9]. Lipids that have been heated repeatedly (during cooking) or stored for long periods of time will break down releasing fatty acids from the glycerides as free fatty acids or FFAs. The rancidity process is a classic example of a lipid breaking down under oxidation. Hence, the amount of free fatty acids (or FFAs) present in an oil is a very important factor determining industrial value. The value is defined based on the ultimate intended use of the product being manufactured and how the lipid chemistry (FFA and/or glyceride present) supports that intended use. From a feedstock's process forgiveness standpoint, green diesel is much more "forgiving" than biodiesel because green diesel processing essentially breaks down the lipid and associated compositional components into simple aliphatic structures. These usually proceed on to catalytic cracking units. Biodiesel must chemically react with lipids while often retaining many of the chemical characteristics of the fatty acid; hence, fatty acid chemistry is much more important to biodiesel.

Table 2 shows the current pricing of primary lipids currently grown within the United States which may be used as lipid feedstocks for both biodiesel and green diesel [15].

Table 2: Feedstock Costs in the United States

Feedstock	Lipid Cost [$/lb.]
Soy	$0.33
Cottonseed	$0.40
Tallow	$0.30
Corn	$0.33
Sunflower	$0.57
Canola	$0.41

The dramatic increase in petroleum prices over the past few months cannot be overlooked as well. As these prices bounce around historically higher ranges, they will continue to fuel the push toward green fuels made from domestic feedstocks which should provide some level of energy independence for the US. However, a recent trend which is somewhat disturbing is the increased presence of imported lipids in the fuels marketplace. Palm oil is the primary source of these imports. It is believed that sometime in the future, importing seed oils will no longer be as easily accepted for receipt of heavy government subsidies, and hence, federal and state government incentives may be reduced or even eliminated. This will only put more pressure on development of domestic lipid sources. Granted, this potential policy shift may cause lipid shortages within some regions. However, it may also stimulate a significantly stronger push toward developing new domestic sources [9].

4. Biodiesel

The Biodiesel industry can actually be considered the most "mature" of the renewable fuels detailed above. Biodiesel production has grown from a niche market in the late 1990's to a large enterprise today. In fact, as recently as 2002, annual domestic production of biodiesel was only in the 25 million gallons per year range [13]. In 2005, the Federal Government dramatically opened up this industry with the promulgation of a $1/gallon blending tax credit that continues today. This Blender credit was joined by Producer credits and tax breaks on installations which sell blends of at least 20% Biodiesel. The result has been a literal explosion of new biodiesel production plants with today's annual production being approximately 700 million gallons per year as estimated by the National Biodiesel Board

[16]. However, estimated diesel usage within the United States is approximately 60 Billion gallons per year; clearly, significant ground must be gained before renewables begin to substantially displace petro-diesel in the United States market [17].

It is estimated that over 85 biodiesel production plants are operating within the United States [16]. This dramatic growth has matured the biodiesel industry away from a critical path tied to expanding markets to one of a growing shortage of lipid feedstocks, or in other words, a feedstock-limited market. However, with that stated, this production rate is only utilizing about half of the estimated national production capacity. Lipid feedstock inventory shortages and the associated high pricing are believed to be the key culprits of this low level of production utilization. Clearly, an increased inventory of reasonably priced lipids with the appropriate chemistry needs to be provided to sustain the growth of this industry [9].

As stated above, the exponential growth of the United States biodiesel industry has basically shifted the industry away from a market concern-based industry to a feedstock-limited concern-based industry. Since the inception of this industry within the United States, soy oil has been the mainstay feedstock of this process, accounting for an estimated 95% of the industry's oil feedstock in the mid-2000's [13]. Note that rapeseed holds this same status within the European markets. The soybean lobby within the United States has essentially built the biodiesel industry as a means of increasing soy oil prices within their historical market, where protein cake was most often the key money-maker.

Over time, new feedstocks have begun to take root within the United States biodiesel market even during the earlier periods when the market was still primarily a market-concerned industry. Beef tallow is an excellent example of the first widespread "shift" within the United States biodiesel industry. With the establishment of the blender's tax credit and resulting boom in the number of biodiesel plants within the United States, soybean prices have dramatically increased soybean commodity prices (essentially more than doubled). Following it were most other lipid resources in the United States including tallow, waste grease, and Canola oil. The resulting shortage of lipids has resulted in two significant changes in the biodiesel industry. The first is a dramatic increase in imported lipids, such as palm oil, which contradicts one of the long-time planks of the developing biodiesel industry's foundation - providing energy independence for the United States. The second is a dramatic increase in the research and commercialization of several "novel" lipid feedstocks such as mustard, algae, bacteria, yeast, sewage sludges, jatrophra, and the Chinese Tallow tree [9-11, 13, 18]. Additionally, it is noteworthy to mention that as green diesel also matures as a viable alternative to petroleum-based diesel, the current lipid shortage is believed to be only further exasperated.

Lipids are used in the biodiesel industry as the major building block of the process. Technically, there are five general methods for producing biodiesel [13, 19]. These methods, in order of descending popularity are:

1. Base catalyzed transesterification
2. Hybrid processing
3. Acid esterification
4. Supercritical esterification
5. Lipase conversion

4.1. Base Catalyzed Transesterification

The most popular biodiesel production method is base catalyzed transesterification which in today's market generally involves the reaction of triglycerides with methanol (an alcohol) and sodium hydroxide (a base) to form a fatty acid methyl ester (FAME) along with the liberated glycerin derived from the triglyceride [20, 21]. Note that the base is actually a catalyst that does not participate in the production of process products; hence, it can be recovered and reused [18]. There has been considerable interest in using ethanol instead of methanol thereby causing many experts to define biodiesel as a fatty acid alkyl ester (both methanol and ethanol are chemically defined as alkyl alcohols). The overall reaction for base catalyzed transesterification via methanol is detailed below [22, 23]:

Lipid (Fats, Oils, or Grease) + Methanol + Base
↓
Fatty Acid Alkyl Ester (FAMES) + Glycerin + Base

The yields are, for every one gallon of lipid input into the system, approximately one gallon of biodiesel is produced [24]. Additionally, on a weight basis, one pound of crude glycerin is produced out of this process for every 10 pounds of biodiesel produced [23]. Pre-2001 or so, glycerin was actually the most marketable aspect of this process and the real "money-maker". However, over time as biodiesel production started to increase resulting in an increasingly glutted glycerin market, this co-product has slipped from money-maker status to a minor co-product that serves as a production cost off-set. In many of today's plants it even serves as a disposal problem [23], with bulk pricing around $0.08-0.09 per pound [25]. Glycerin can refined into a pharmaceutical-grade product; however, most plants are not willing to spend the high capital costs of adding this additional processing, particularly given concerns over the stability of the glycerin market. Hence, few biodiesel plants are producing pharmaceutical grade glycerin. Some glycerin refiners in early 2011 even stopped accepting shipments of 80% crude biodiesel glycerin, citing purification costs and market saturation [25]. A growing interest area within the biodiesel industry is the development of increased industrial uses of glycerin produced at biodiesel plants with hopes of returning some level of profitability to glycerin (much like DDG adds to corn-based ethanol production). One such product is the conversion of glycerin to mono propylene glycol. With a larger potential market and bulk prices averaging $0.20-0.30 per pound higher than purified glycerin, it could potentially be a valuable co-product [26].

Lipid sources that are available often are not simply composed of just triglycerides that follow the reaction presented above. Virgin oils (particularly from seed sources) typically do contain almost exclusively triglycerides. However, secondary processed oils such as rendered animal fats and waste grease often contain a significant level of FFAs. When reacted within a base catalyzed transesterification system these are actually converted to soapstock [27]. Therefore, as FFA levels begin to exceed 10% (some use 5%), then the overall economic feasibility of using base catalyzed transesterification diminishes [13, 28]. Hence, the second biodiesel production method listed above may be an option. This process is discussed is Section 4.3 because it utilizes both base catalyzed transesterification and acid esterification.

4.2. Acid Esterification

This process is highly applicable with FFAs, but very rarely used with triglyceride-laden oils [29]. Currently, it is not a very popular process since there are few FFA-only feedstocks used in the industry. The overall reaction is presented as [13, 27]:

$$\text{Free Fatty Acid (FFA)} + \text{Alcohol} + \text{Acid} \\ \downarrow \\ \text{Biodiesel (FAME)} + \text{Water}$$

Note that glycerin is not liberated in the above reaction since it is not present within a system of only FFAs. Usage of this process as a stand-alone system is not very common due to the limited supply of feedstock amendable to this type of processing. The reaction kinetics for FFAs within an acid catalyzed esterification system are rapid, yet the conversion of triglycerides is kinetically very slow. However, as lipid inventories dwindle and prices increase, several non-traditional FFA-based streams such as tall oil may increase investment in acid esterification processing. Other potential feedstocks that are good fits for acid catalyzed esterification are yellow grease (>75% FFAs) and FFAs generated at acidulators which convert gumming residuals from oil purification activities back into FFA-based liquids. The key negative aspect of this process is that it is kinetically extremely slow to convert triglycerides, which essentially makes it not very practical for use with oils that contain little to no FFAs.

4.3. Hybrid Processing

The hybrid process is actually a combination of acid catalyzed esterification and base catalyzed transesterification [13]. The two are run in series where the acid stage is performed first allowing the FFAs present to be converted via a kinetically rapid reaction. The triglycerides remain fairly unreacted. Then, the unreacted triglycerides are converted into FAMEs via the base catalyzed step, which is also a kinetically rapid step. This process is perfect for multiple feedstocks with mixed FFA and whole triglyceride contents. As lipid supplies dwindle and associated prices increase, biodiesel producers do not have the luxury of simply processing virgin oils and in fact are often combing the lipid markets for reasonably priced feedstocks. Often times this results in a situation where high FFA content lipids are processed. This high level of processing flexibility has shifted a lot of recent purchases of biodiesel processing equipment toward this option; however, if a facility is reasonably sure that minimal amounts of FFA-laden feedstocks will be processed within the plant over time, then the capital investment directed toward the acid processing aspect is likely a wasted investment. The resources required may be better utilized for increasing base catalyzed processing capacity.

4.4. Supercritical Esterification

This is a developing process option in which supercritical conditions within highly specialized reactors, capable of safely supporting high pressure and temperatures, are used to produce FAMEs. In fact, both FFAs and triglycerides are very rapidly processed within the same reactor using the same process chemistries [30]. The Japanese have been the pioneers of this method, yet some United States entities are beginning to consider this processing option due to the capability to process highly differing lipid feedstocks within a fairly small footprint. Obviously, processing costs are higher and system complexities are much more intense when compared to the other processing options discussed thus far. This is still very much a developing process with neither operational or capital costs well-defined. It will be interesting to observe how this process develops; particularly when compared to the costs of the hybrid process since both processes can handle mixed lipid streams (whole oil and FFAs).

4.5. Lipase Processing

This is a very immature process that is a research topic gaining significant international interest [31-34]. In this system, biotic enzymes are used to perform the transesterification reactions of triglycerides [33]. Given its highly immature state of development, there are no known facilities of any scale using this process. However, the research does show promise and the activity levels associated with its development by research groups do seem to be rapidly increasing. The key advantage of this process is that a relatively low energy input is required to produce the FAME; however, the kinetics and completeness of these reactions do appear to be limiting [35].

4.6. Other Lipid Chemistry Impacts

Not only does the level of FFAs present in a given lipid impact the processing efficiency and costs associated with the production of biodiesel, but other chemical factors can also greatly contribute to fuel quality, acceptability, processing requirements, and cost. The two most commonly considered chemistry characteristics are the degree of saturation and water content. However, fatty acid geometric shape (straight chained versus branched), carbon number, and the presence of other saponifiable lipids, such as the level of phospholipids present, all are believed to have some impact on the final product.

The degree of saturation is the most critical and discussed issue among the biodiesel industry because it can directly impact one key characteristic - cold flow. As the level of saturation increases, the pour point (a measure of cold flow properties) increases. This means that a biodiesel composed of a significantly high degree of saturation will very likely have issues with crystallizing during transit through colder climates. A prime example is bacon grease hardening at room temperature as compared to corn oil remaining liquid at the same temperature. A typical rule of thumb is that a lipid with a degree of saturation greater than 35% may have poor cold flow properties in terms of use as a fuel.

Water is often a consideration due to the impact of free water present on the economics of biodiesel processing. Excess water requires an additional separation step to recover the glycerin and methanol. This extra processing adversely impacts processing costs.

The amount of phospholipids present in the oil also may be an issue for most biodiesel production facilities. Phospholipids are typically composed of a glycerin backbone with only two fatty acids attached and a carbo-phosphorus link on the second or third position. Since many of the oil feedstocks used are degummed prior to sale, and because degumming does remove phospholipids, the presence of these compounds are rarely an issue in using most seed oils. However, as novel feedstocks are explored such as living microorganisms (bacteria, yeast, and algae) or meat products (cow brains, beef processing residuals, etc.), then the presence of phospholipids may be a consideration. Many microbes, such as bacteria and algae, may be composed on significant percentages of phospholipids, thereby becoming a basis for concern. The exact impacts have not really been explored except that phospholipids typically have one saturated fatty acid and one unsaturated fatty acid attached making the overall degree of saturation 50%. The fate of the carbo-phosphorus within processing reactions is also not well-known. One interesting aspect is that there do appear to be some markets for the molecule if it is extracted intact. Additionally, since phospholipids are fairly polar then extraction of phospholipids via traditional, non-polar chemical extraction fluids such as hexane will be minimal. This may resolve concerns, but also limit the extent of lipids available for processing (assuming it is found that phospholipids are not a concern). Conversely, if more polar extractants are used as stand-alone extracts or part of a co-solvent extraction fluid, such as the use of acetone and/or methanol for rupturing cells, than the presence of phospholipids and their impacts should be considered. However, as stated above, the issue of phospholipids being present in the feedstock is viewed as one to be considered only if problems with their biodiesel production are reported and/or observed.

4.7. Biodiesel Production Costs

As with any commodity chemical production, the profitability level associated with the product over a reasonable term is absolutely critical to the overall stability of the industry. In the case of biodiesel, feedstock inventories and associated costs have provided an economic "roller coaster" for investors. A mass and economic balance for the production costs of biodiesel via the transesterification process is estimated for this paper by using production data generated from a variety of sources [13, 15, 36]. These costs are presented using a series of ranges to illustrate the impact of process inputs on the total production cost range (note that any profitability associated with glycerin is not included in this estimate):

From above, note that the cost of the feedstock represents over 80% of the total processing cost [13, 36]. Thus, this one aspect (oil price) has emerged as the key consideration when performing due diligence of a potential construction project for a biodiesel plant. Many times during discussions with potential investors in biodiesel plants the authors have noted that investors assumed sufficient lipids will be regionally available for their long-term use. The recent demand for lipids has made this assumption one that may result in significant future production problems [6]. Additionally, many more recent conversations between the authors and other investors indicate that they are focusing on imported lipids due to difficulties in locking competitive domestic feedstock prices and/or volumes. This is a troubling trend given that it is a national goal to use biofuels as a means of moving the United States toward increased energy independence.

Table 3: Biodiesel Production Costs

	Cost per gallon of Biodiesel
Feedstock	\$2.00-\$3.20
Processing	\$0.20-\$0.40
Shipping	\$0.10-\$0.40
Other	\$0.20-\$0.40

It is also interesting to note that finding a buyer of produced biodiesel has slowly been reduced among concern priorities when evaluating project feasibility due to recent federal and state incentives and mandates. This is a significant industry shift given that this was the key issue as recently as 2003.

A more detailed mass balance of chemical feeds, products, and catalysts for the production of biodiesel using base catalyzed transesterification can be described as follows [21]. One-hundred pounds of lipids and 20 pounds of methanol will produce 100 pounds of biodiesel, 10 pounds glycerin, and 10 pounds of excess methanol. One pound of base catalyst is used in the procedure, with a recovery of almost 100\% possible. Hence, a biodiesel plant using the base-catalyzed transesterification process must ensure that approximately 130,000 gallons of methanol be made available for every million gallons of biodiesel produced (assuming a reasonable recovery rate of the excess methanol).

Three other significant impacts to the cost of producing biodiesel have recently emerged. The first is the competition for lipids imposed by the developing green diesel industry, discussed in Section 5. This new industry is being implemented at existing refineries thereby placing biodiesel facilities in direct competition with large oil companies for lipid feedstocks. This is actually a great situation for algae farms, but not for independent biodiesel producers. The second costs are those associated with the greatly increased price of methanol. The traditional cost of methanol has been in the high sub-one dollar range for many years. The cost of methanol is currently hovering around $1.20-1.40 per gallon over the past 12 months [37]. However, in 2007 it had spiked to well over $2.00 per gallon before falling again. The third and final cost issue is the increased cost of product transportation associated with increasing petroleum prices. This issue is somewhat good news for the biodiesel industry because it fuels public support for their product, yet it does adversely impact production costs due to increased costs associated with the transport of feedstocks and products to buyers.

5. Green Diesel

Although some properties of petroleum diesel and biodiesel are similar, the molecular structure is vastly different. While this is good enough for blending with petroleum diesel in small quantities, blends higher than 20% may require engine modification [16]. There are also other problems with biodiesel's compatibility, such as not being able to transport it over existing petroleum pipelines and the need to construct new plants if production capacity is to be dramatically increased. In contrast, a fuel made from renewable feedstocks but with the same molecular structure as petroleum diesel would be a much better match. Green diesel, sometimes also known as renewable diesel or biocrude, fits this role by being chemically similar to petroleum diesel. The green in its name comes from the renewable nature of its feedstock. It is produced through cracking of lipids, the products of which are chemically very similar to petroleum diesel. This allows for a blending of up to 100% with standard petroleum diesel. The similarity with petroleum diesel also means that cold flow problems associated with biodiesel are eliminated. In addition, it may be possible to crack non-lipid feedstocks and produce a fuel with the qualities of green diesel. The ability to use existing infrastructure for renewable fuel production, combined with superior blending, make up green diesel's main benefits as compared to biodiesel. Since the fuel is chemically very similar to petroleum diesel the emissions characteristics are also similar. This is mitigated due to the renewable source of the feedstocks.

Initial research with green diesel concentrated on products obtained from thermal catalytic cracking (pyrolysis) of biomass. Such products are often referred to as bio-oil, and contains compounds such as organic acids, alcohols, aldehydes, ethers, esters, ketones, furans, phenols, hydrocarbons, and other non-volatile components [38]. A major benefit of bio-oil was the wide range of feedstocks which could be used. Anything from chicken fat to wood chips could be turned into a liquid fuel. Overall, however, bio-oil is considered a poor substitute for conventional fuels due to its low BTU value and incompatibility with existing engines [39]. Thermal cracking also requires high temperatures which increase production costs. One reason for the large variety of products obtained from biomass pyrolysis is the complex structure of the feedstock. Plant and animal oils consist of long hydrocarbon chains terminated with esters and carboxylic acids. Cracking of these renewable oils could produce a variety of long-chain hydrocarbons chemically similar to petroleum diesel [40]. Research on thermal cracking of natural oils has shown that the products consist mainly of C_4-C_6 aromatic and aliphatic hydrocarbons, C_2-C_4 olefins, hydrogen, and a fraction similar to that of petroleum diesel [41]. The final product is known as Bio-oil. However, this requires high temperatures in the range of 300-500 °C with little control over the final products [41, 42]. Selectivity of the cracking process is therefore limited, possibly reducing final yields.

5.1. Green Diesel Production and Processing

The use of catalysts to catalytically crack lipids was first brought to the attention of scientists in 1979 by researchers at Mobil [43]. Although the ability to thermally depolymerize biomass (thermal cracking) was known for some time, the use of superacids to produce diesel-range compounds allows for a temperature reduction to 150-200 °C. It also enables a more controlled cracking than pyrolysis [39]. This gives a product with better characteristics than bio-oil, such as improved viscosity and energy density, although solid biomass such as wood scraps could not be used. In comparison to bio-oil, however, the cracking of lipids offers a smaller range of products than those obtainable through pyrolysis. This comes at the trade-off of larger molecular weights. Reaction mechanisms proposed in literature show the cracking of lipids to follow a fairly linear path, with few possible branches [38]. It begins with fatty acids and esters undergoing either decarboxylation or deoxygenation. If a catalyst is used which favors decarboxylation, the products will be a variety of hydrocarbon gases and carbon dioxide. A deoxygenating catalyst will produce mixtures of aldehydes and ketones, which are further cracked to aromatic hydrocarbons, hydrocarbon gases, and coke. In practice, a mix of different pathways is used to produce green diesel fuel. Studies have shown that temperature plays a vital role in product distribution with the use of superacid catalysts, with lower temperatures producing larger amounts of aliphatic hydrocarbons [40, 44].

Although large-scale processing of animal and plant fats in petroleum refineries is a relatively recent trend, energy companies are not wasting any time in adopting the technology. In 2007, ConocoPhillips and Tyson Chicken begun to explore partnership to "produce a new type of diesel fuel made from beef, pork, and poultry fat" [45]. Neste Oil is a European company with several green diesel facilities. They recently began construction on a dedicated green diesel plant in Rotterdam which will produce 800,000 metric tonnes of diesel per year upon completion [46]. Other companies currently employing the technology include Petrobras in Brazil, Syntroleum in the United States, and UOP-Eni in the United States and Italy. As mentioned earlier all lipids have a similar structure, especially compared to the wide range of compounds in bio-oil. While the composition of lipids from different sources can vary wildly, it will always contain some type of fatty acid. This translates to a cracking product stream which is remarkably similar across different lipid sources [47]. Such similarity helps reduce the capital cost needed for processing different feedstocks and insures a stable product stream.

Although it is possible to create a diesel fraction at lower temperatures than bio-oil, green diesel is often co-fed into a hydro-treating reactor with standard petroleum. The reaction is therefore carried out at around 300-400 °C. Refineries already use hydro-processing to remove impurities such as sulfur and nitrogen [48]. Existing equipment can therefore be used to process lipid streams with a minimum of additional capital cost. Under hydro-treating conditions a lipid triglyceride is converted into a minimum of four molecules, three long chain hydrocarbons and a propane molecule. This propane molecule is the remnant of a triglyceride's glycerol backbone. Water and CO_2 are also produced, with reaction times typically between 10 to 60 minutes. Tuning the reaction parameters can give a yield of over 90% diesel fraction when hydrotreating lipids [49]. DOE estimates that the energy requirement for producing one pound of green diesel is 1,900 Btu. This is 10% less than the energy required for soybean lipid conversion to biodiesel. A life cycle analysis using DOE's GREET model shows that production of green diesel consumes 8.6% less energy than biodiesel (mmBtu basis) [49]. Emissions from green diesel are also lower than that of petroleum diesel. Calculated lifetime emissions for soy based green diesel were calculated at 44% of petroleum diesel, compared to 59% for soy biodiesel [50].

Even though lipids can be co-fed with petroleum diesel in an existing refinery, some companies are building dedicated green diesel plants. Syntroleum recently partnered with Tyson foods for production of green diesel and jet fuel [51]. Groundbreaking on a new plant took place in October of 2008 in Geismar, Louisiana. The projected cost is $138 million for a 75 million gallon per year plant, fed by low-grade lipid feedstocks. ENI has also started construction on a 95 million gallon per year plant in Italy [52]. Neste Oil began construction in 2009 of a 250 million gallon per year green diesel plant in Rotterdam, at a cost of $940 million USD [46].

The most critical data yet to be fully disclosed by the technical community is the actual cost on a per gallon basis for green diesel. General reports from presentations being made do infer that green diesel will cost approximately the same as biodiesel. Discussions with experts also indicate that these estimates appear to be correct [53]. Our literature review substantiates this speculation. Clearly, the cost will be dependent on feedstock costs. It is concerning that detailed pricing of processing costs have not yet emerged, but it expected that these figures will emerge as the process continues to gain momentum as a viable national fuel option. Suffice it to state that the authors do feel confident in stating that the current estimates of similar production costs to biodiesel are likely reasonably correct. Issues yet remain in terms of developing more concrete costs, such as the allowance of green diesel to also receive federal tax credits (rulings continue to gravitate back and forth over the allowing of green diesel to receive the blenders credit). The opinion of the authors is that the federal government should provide such tax benefits to any renewable fuel that does truly utilize biomass or any other renewable, eco-neutral feedstock to produce adequately performing fuels.

Green diesel does appear to have many advantages over the other bio-based diesels. Some of these potential advantages are summarized below:

1. The process utilizes existing refining operations thereby eliminating the need for the immense capital investment required in the United States to produce a significant amount of biodiesel capable of truly displacing significant amounts of petroleum diesel.

2. The fuel is produced by refineries with a long track record of safely producing high grade products thereby eliminating the uncertainty of a fuel produced by a large number of independent producers with limited experience in fuels production.

3. The producers can utilize existing transportation and storage capacity (pipelines, tankage, trucks, etc.) thus eliminating the need for establishing a separate system. It should be noted that due to the detergent character of biodiesel, it cannot be transported or stored in existing petroleum facilities.

4. This industry places production of a fuel in the hands of companies with significant experience with the marketing and distribution of fuel products.

5. The process utilizes a high portion of the lipids, such as the glycerin conversion to propane.
6. Existing refineries will be able to convert other components found in many lipid feedstocks, such as FFAs, waxes, and carbohydrates that are not well suited for use within most biodiesel production plants.
7. Currently green diesel appears to have similar processing cost as biodiesel.
8. Capable of producing a well-performing product even when using highly saturated lipids/FFAs.
9. The resulting fuel appears to have more stable fluid and burn properties at low temperatures than FAMEs.
10. The process is very forgiving in terms of lipid or lipid constituent which may be used as a feedstock to the process.

The track record of producing this product within refineries is still in its early stages due to its relative immaturity on the commercial scale. Early reports are favorable as detailed within the listing above. There are, however, some drawbacks to green diesel use and production. In order to turn lipids into hydrocarbon the hydro-treaters must have a constant supply of hydrogen. This is currently supplied from petroleum, which stops green diesel from becoming fossil-fuel independent. One way to get around this limitation is production of hydrogen through microbial action, which is in itself a current research topic [54]. Use of hydrogen from syn-gas streams has also been proposed as a renewable alternative. While several demonstration plants have been built, the technology is not yet ready for commercialization. Another potential problem is poisoning of hydro-treating catalysts by compounds brought in with lipid feedstocks. Research has shown that trace elements such as phosphorus, present in some lipid sources, interfere with the cracking process [55, 56]. This causes lower yields and poor quality fuel. Work concerning phosphorus is important because many micro-organism based lipids under development, such as bacteria, yeast, and some algae, may contain appreciable levels of phospholipids which can have significant phosphorus present. This could potentially be a larger concern than with Biodiesel.

6. Implications of a Potential Dual Market

There has been considerable discussion and, quite frankly, a lot of hot debate over the emergence of green diesel. Its maturation as a viable market may impact years of effort to commercialize biodiesel [57]. In many respects, the debate may stem from concerns by the biodiesel industry that with similar costs of production and a more forgiving feedstock, green diesel may become the fuel of choice. However, as one reviews the benefits of each fuel, biodiesel does have a future. This is particularly true within regions not having refining capacity or the tonnage of oil sufficient enough to sustain a refinery. Albeit, the allowance of green diesel within the current liquid fuels distribution system and the potential for direct competition for lipids by the larger energy companies against the smaller biodiesel plants does present some serious issues for the biodiesel industry. The smaller biodiesel plants are typically stand-alone investments provided by independent investors, without the resources of large refineries. It is often stated that any truly viable industry must strive toward true profitability that is not totally based on long-term government incentives or subsidies. Hence, both industries must strive toward deducing actual production costs along with finding increased feedstock volumes and reduced feedstock costs. With careful utilization of the benefits in each fuel, a dual market may emerge. Clearly, for small producers such as localized farming Co-OPs and home producers, biodiesel will remain as the most viable option. If green diesel emerges as the only renewable fuel, then the higher priced oils may experience a reduced market share compared with traditionally lower cost lipid feedstocks such as tallow, palm oil, Chinese tallow, and tall oil. This scenario may occur because the higher-priced oils tend to have lipid chemistries ideal for biodiesel production. The high degree of carbon bond saturation with cheaper oils typically makes poor biodiesel, but is a good feedstock for green diesel. However, the emergence of green diesel may not be the only potential competitor to biodiesel. As GTL technology matures, and if a resulting decrease in production costs results, this even more feedstock-forgiving/tolerance technology may become the primary fuel of choice sometime in the future. The possibility of a three-way competition for resources may loom around the corner.

7. Conclusions

The future of renewable diesel products that have potential to significantly reduce petroleum dependence appears to be both bright and volatile. Various technologies are rapidly maturing and the demands on the various potential feedstocks may change dramatically as markets react to technological improvements. Biodiesel is by far the most mature within the many options of renewable diesel fuels that are either developed or developing. The simplicity of its processing coupled with a broad range of processing scales which can be used for contribution to the overall national energy reserves is very positive. The range of scale lends itself directly to use in poorer areas and smaller installations, increasing the availability of fuel to wider populations. However, it does face some aspects of direct competition, particularly with green diesel. While green diesel has more technology verification and maturation before it becomes a prime fuel option, its potential to outcompete biodiesel is apparent. Broad fuel compatibility combined with established and well-funded production plants are giving green diesel a head start in commercialization and competitiveness. In any case, the agriculture industry will very likely be the key provider of feedstocks regardless of the technology that emerges. Additionally, particularly in the case of both green diesel and GTL fuels, the potential does exist for the use of waste materials as additional feedstocks to the production of a renewable diesel product; which would address both energy demands and waste management needs. Clearly, as developments and financial investments continue, the nation appears to be positioning itself toward increased energy independence while providing a more ecological friendly fuel.

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References

[1] S. Butler and K. Holmes. Twelve Principals to Guide US Energy Policy, volume Backgrounder No. 2046. The Heritage Foundation, Washington DC **(2007)**.
[2] K. Verschueren. Handbook of Environmental Data on Organic Chemicals. Van Nostrand-Reinhold Pub. **(1983)**.
[3] T. Kita-Borsa, D. Pacas, S. Selim and S. Cowley. Ind. Engr. Chem. Res., 37, pp. 3366–3374, **(1998)**.
[4] H. Huo, M. Wang, C. Bloyd and V. Putsche. Life-Cycle Analysis of Energy and Greenhouse Gas Effects of Soybean-Derived Biodiesel and Renewable Fuels. Technical Report ANL/ESD/08-2, USDOE **(2008)**.
[5] D. Coltrain, editor. Biodiesel: Is it Worth Considering?, Risk and Profit Conference. Kansas State University, Manhatten, Kansas **(2002)**.
[6] T. Durret, C. Benning and J. Ohlrogge. Plant Journal, 45, pp. 593–607, **(2008)**.
[7] F. Armstrong. Biochemistry. Oxford University Press Inc., New York, NY **(1989)**.
[8] M. Wenk. Nature, 4, pp. 594–610, **(2005)**.
[9] S. Dufreche, R. Hernandez, T. French, D. Sparks, M. Zappi and E. Alley. J. American Oil Chemist Society, 84, pp. 181–187, **(2007)**.
[10] R. Subramaniam, S. Dufreche, M. Zappi and R. Bajpai, Food Technology and Biotechnology, 48, 3, pp. 329–335, **(2010)**.
[11] S. Ayalasomayajula, R. Subramaniam, A. Gallo, S. Dufreche, M. Zappi and R. Bajpai., Ind. Eng. Chem., **(2011)**, doi:10.1021/ie201000s.
[12] U. E. R. Service. Oil Crops Situation and Outlook Yearbook. Technical Report OCS-2002, US Department of Agriculture **(2002)**.
[13] M. Zappi, R. Hernandez, D. Sparks, J. Horne, M. Brough, S. Arora and D. Motsenbocker. A Review of the Engineering Aspects of the Biodiesel Industry. Technical Report MSU E-TECH Laboratory Report ET-03-003, Mississippi Biomass Council **(2004)**.
[14] B. I. Inc. Sales Brochure **(2008)**.
[15] U. E. R. Service. Oil Crops Outlook: Dec 2008. Technical Report OCS-08K, US Department of Agriculture **(2008)**.
[16] N. B. Board. Informational Brochure - 2009 US and Canada Plant Map. Washington DC **(2009)**.
[17] C. Peterson. Potential Production of Biodiesel. Technical report, University of Idaho Department of Biological and Agricultural Engineering **(2008)**.
[18] M. Devanesan, T. Viruthagiri and N. Sugumar. African Journal of Biotechnology, 6, 21, pp. 2497–2501 **(2007)**.
[19] G. Knothe, R. Dunn, and M. Bagby. Biodiesel: The Use of Vegetable Oils and Their Derivatives as Alternative Diesel Fuels. Technical report, National Center for Agricultural Utilization Research, USDA **(2007)**.
[20] J. Bozell. In Transition to a Bioeconomy Integration of Agriculture and Energy Systems. Atlanta, GA **(2008)**.
[21] O. Alamu, T. Akintola, C. Enweremadu and A. Adeleke. Scientific Research and Essay, 3, 7, pp. 308–311 **(2008)**.
[22] J. Cervero, J. Coca and S. Luque. Grasas Y Aceites, 59, 1 **(2008)**.
[23] D. Pyle. Use of Biodiesel-Derived Crude Glycerol for the Production of Omega-3 Polyunsaturated Fatty Acids by Microalga Schizochytrium limacinum. Master's thesis, Biological System Engineering, VaTech University **(2008)**.
[24] UT-Knoxville. Economic Feasibility of Producing Biodiesel in Tennessee. http://web.utk.edu/aimag/pubs/biodiesel.pdf, **(2002)**.
[25] J. Taylor. Glycerine (USA) Price Report. ICIS Pricing Report **(2011)**.
[26] L. Wong. Mono Propylene Glycol (USA) Price Report. ICIS Pricing Report **(2011)**.
[27] R. Babcock, E. Clausen, M. Popp and W. Schulte. Yield Characteristics of Biodiesel Produced from Chicken Fat-Tall Oil Blended Feedstocks. Technical Report Completion Report MBTC-2092, University of Arkansas **(2007)**.
[28] B. Freedman, E. Pryde, and M. T.L. J. of the American Oil Chemists' Society, 61, 10, pp. 1638–1643, **(1984)**.
[29] F. Ma and M. Hanna. Bioresource Technology, 70, pp. 1–15, **(1999)**.
[30] L. Tavlarides, G. Anitescu, A. Deshpande and P. Rice. Integrated Multistage Supercritical Technology to Produce High Quality Vegetable Oil and Biofuels. Technical Report 01274-001-01, Syracuse University **(2006)**.
[31] C. Tao and B. He. Transactions of the American Society of Agricultural and Biological Engineers, 49, 6, pp. 167–174, **(2006)**.
[32] X. Zhao, B. El-Zahab, J. Perry and P. Wang. Journal of Applied Biochemistry and Biotechnology, 143, pp. 236–243, **(2007).**

[33] Y. Huang and Y. Yan. Lipase-catalyzed Biodiesel Production with Methylene Acetate as Acyl Acceptor. Depart-mental published abstract, school of life science and technology, Huazhong Institute of Technology, Wuhan, China **(2007)**.
[34] D. Cowan, K. Oxenball and H. Holm. Oil Mill Gazetter, 113 **(2008)**.
[35] S. Al-Zuhair. Biotechnology Progress, 12, pp. 1442–1448, **(2005)**.
[36] M. Haas, A. McAloon, W. Yee and T. Foglia. Bioresource Technology, 97, pp. 671–678, **(2006)**.
[37] Methanex. Historical Methanex Posted Prices. http://www.methanex.com/products/documents/MxAvgPrice_Oct282011.pdf, **(2011)**.
[38] J. D. Adjaye and N. N. Bakhshi. Biomass and Bioenergy, 8, pp. 131–149, **(1995)**.
[39] N. G. Wilson and P. T. Williams. International Journal of Energy Research, 27, pp. 131–143, **(2003)**.
[40] S. P. R. Katikaneni, J. D. Adjaye, R. O. Idem and N. N. Bakhshi. Industrial and Engineering Chemistry Research, 35, pp. 3332–3346, **(1996)**.
[41] R. O. Idem, S. P. R. Katikaneni and N. N. Bakhshi. Energy and Fuels, 10, pp. 1150–1162, **(1996)**.
[42] F. Billaud, T. Minh, A. K., P. Lozano and D. Pioch. Journal of Analytical and Applied Pyrolysis, 58-59, pp. 605–616, **(2001)**.
[43] P. B. Weisz and et al. Science, 206, pp. 57–58, **(1979)**.
[44] S. P. R. Katikaneni, J. D. Adjaye and N. N. Bakhshi. Energy and Fuels, 9, pp. 599–609, **(1995)**.
[45] R. Baum and ConocoPhillips. Chemical and Engineering News, 85 17, 25, **(2007)**.
[46] N. Oil. NesteOil builds Europe's largest renewable diesel plant in Rotterdam. http://www.nesteoil.com/default.asp?path=1;41;540;1259;1260;11736;12695, **(2009)**.
[47] T. A. Milne, R. J. Evans and N. Nagle. Biomass, 21, pp. 219–232, **(1990)**.
[48] R. Sadeghbeigi. Fluid Catalytic Cracking Handbook. Gulf Publishing Company, **(2000)**.
[49] DOE. GREET 1.8c.0 Fuel Cell Model. http://www.transportation.anl.gov/modeling_simulation/GREET/ **(2009)**.
[50] R. D. S. of the WSDA Technical Work Group. Renewable Diesel Technology. http://www1.eere.energy.gov/cleancities/toolbox/pdfs/renewable_diesel_white_paper_final.pdf, **(2007)**.
[51] Syntroleum. Initial Construction Underway on Dynamic Fuels Plant, **(2009)**.
[52] ENI. UOP and Italy's ENI Announce Plans for Facility to Produce Diesel from Vegetable Oil. http://www.uop.com/pr/releases/PR.EniEcofiningFacility.pdf, **(2007)**.
[53] S. Tyson. Personal discussions with Dr. Shane Tyson, noted biofuels expert, **(2007)**.
[54] T. Milne, C. Elam, and R. Evans. Hydrogen from Biomass: State of the Art and Research Challenges. Technical Report IEA/H2/TR-02/001, NREL DOE, **(2002)**.
[55] C. S. Chen and S. E. Schramm. MicroporousMaterials, 7, pp. 125–132, **(1996)**.
[56] S. Dufreche. Effect of Phosphorous Poisoning on Catalytic Cracking of Lipids for Green Diesel Production. Ph.D. thesis, Mississippi State University, **(2007)**.
[57] R. Kotrba. Biodiesel magazine, **(2008)**.

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