

# Processing of Soybean Oil into Fuels

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## 1. Introduction

### 1.1 Rationale for processing soybean oil into a fuel

Abundant and easily refined, petroleum has provided high energy density liquid fuels for a century. However, recent price fluctuations, shortages, and concerns over the long term supply and greenhouse gas emissions have encouraged the development of alternatives to petroleum for liquid transportation fuels (Van Gerpen, Shanks et al. 2004). Plant-based fuels include short chain alcohols, now blended with gasoline, and biodiesels, commonly derived from seed oils. Of plant-derived diesel feedstocks, soybeans yield the most of oil by weight, up to 20% (Mushrush, Willauer et al. 2009), and so have become the primary source of biomass-derived diesel in the United States and Brazil (Lin, Cunshan et al. 2011). Worldwide ester biodiesel production reached over 11,000,000 tons per year in 2008 (Emerging Markets 2008). However, soybean oil cannot be burned directly in modern compression ignition vehicle engines as a direct replacement for diesel fuel because of its physical properties that can lead to clogging of the engine fuel line and problems in the fuel injectors, such as: high viscosity, high flash point, high pour point, high cloud point (where the fuel begins to gel), and high density (Peterson, Cook et al. 2001).

Industrial production of biodiesel from oil of low fatty-acid content often follows homogeneous base-catalyzed transesterification, a sequential reaction of the parent triglyceride with an alcohol, usually methanol, into methyl ester and glycerol products. The conversion of the triglyceride to esterified fatty acids improves the characteristics of the fuel, allowing its introduction into a standard compression engine without giving rise to serious issues with flow or combustion. Commercially available biodiesel, a product of the transesterification of fats and oils, can also be blended with standard diesel fuel up to a maximum of 20 vol.%. In the laboratory, the fuel characteristics of unreacted soybean oil have also been improved by dilution with petroleum based fuels, or by aerating and formation of microemulsions. However, it is the chemical conversion of the oil to fuel that has been the area of most interest. The topic has been reviewed extensively (Van Gerpen, Shanks et al. 2004), so this aspect will be the focus in this chapter. Important aspects of the chemistry of conversion of oil into diesel fuel remain the same no matter the composition of

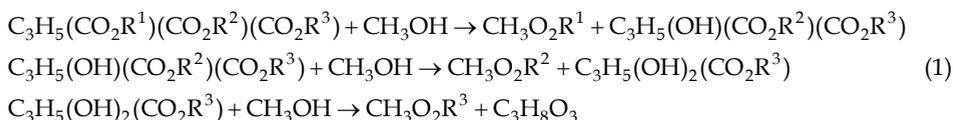
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the triglyceride. Hence, although the focus in this book is on soybean oil, studies on other plant based oils and simulated oils have occasional mention in this chapter. Valuable data can be taken on systems that are simpler than soybean based oils, with fewer or shorter chain components. Sometimes the triglycerides will behave differently under reaction conditions, and when relevant, these have been noted in the text.

## 1.2 Transesterification and homogeneous base catalysis

Processing of soybean oil into a diesel compatible fuel through transesterification has received much recent attention as the most likely route to large-scale adoption of bio-based diesel. To improve flow characteristics, the triglyceride that constitutes the soybean oil has to be broken apart into smaller molecules. Fragmentation of the triglyceride takes place through a transesterification mechanism, a three step process that yields a molecule of esterified fatty acid at each step, shown below in Reaction (1) (Freedman, Pryde et al. 1984). Initially, the soybean oil reacts with a molecule of methanol, in the form of a reactive methylate in the case of base catalysis, to cleave a long-chain fatty acid fragment from the glycerine backbone that becomes a methyl ester, depicted as  $R^1$  in the reaction below. The residual chains ( $R^2, R^3$ ) attached to the backbone comprise a diglyceride after the first step, a monoglyceride after the second step, before the final decomposition to glycerine, or 1,2,3-propanetriol, and an ester at the last step. Commercially, a base such as sodium hydroxide or methylate is used to catalyze the transesterification process, promoting the reaction between the alcohol and the oil.



Triglyceride + 3 Methanol  $\rightarrow$  3 Methyl Esters + Glycerine

In commercial parlance, the glycerine that is produced by transesterification is termed free glycerine, and the unreacted tri-, di-, and monoglycerides are called bound glycerine, usually expressed as wt.%. The base catalyst is usually introduced as anhydrous sodium methylate, to minimize the amount of water in the system as this leads to saponification, Reaction (2). The amount of base catalyst typically used is only slightly over 1 vol.% of the methanol, again to reduce formation of soapy emulsions. While the stoichiometry of the process demands a mole ratio of methanol to oil of 3, commercially the ratio is doubled to push the reaction to completion. In the US, biodiesel must have a bound glycerine content of less than 0.24 wt.% and a free glycerine content of less than 0.3 wt.% to be sold commercially. Standards for biodiesel purity are based either on the removal of contaminants before the oil feedstock is esterified or on the separation of unwanted by-products (ASTM 2007; ASTM 2008).

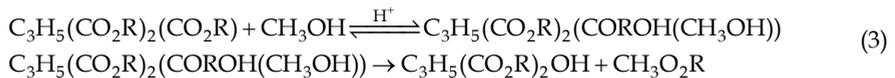


Methanol and base catalyst (in the form of NaOH or sodium methylate) are the reagents of choice in industrial production because of their being less expensive than other reagents. Potassium hydroxide has the advantage of a lower rate of saponification. Other alcohols can be used, primarily ethanol. Longer chain alcohols have better miscibility with the oil and

hence higher yields, however, the product esters also become more difficult to separate from glycerine.

### 1.3 Esterification and homogeneous acid catalysis

The conversion of fatty acids to esters can also be catalyzed by acids in the esterification reaction scheme shown in Equation (3). The mineral acids commonly used as catalysts include sulfuric or hydrochloric acid. This chemical route is less popular when working with good quality soybean oil as a feedstock, because of the low free fatty acid content of the oil. For degraded or lower quality feedstocks, however, the advantages of avoiding large amounts of bound and free glycerine production as happens during transesterification can be desirable. Before triglycerides can be subjected to esterification, they must be saponified using base, such as NaOH, to strip apart the acylglyceride chains. Treatment with acid follows to protonate and form fatty acids. In the expression (3) below, the acid allows a complex to form between the triglyceride and the alcohol, which then falls apart to give a methyl ester and the diglyceride. Similarly to transesterification, the reaction progresses sequentially through a number of steps, not all shown in (3).



### 1.4 Conventional processing of soybean oil into methyl esters

Vegetable oils, including soybean oil, have complex compositions, which include a variety of fatty acid chain lengths. Soybean oil consists primarily of palmitic, oleic, linoleic, and linolenic acid chains, with a typical mixture given in Table 1 (Holčapek, Jandera et al. 2003). The actual composition depends on the source of the oil and can vary from one variety to another (Mello, Pousa et al. 2011). In addition to the variation in the fatty acid chains linked to the glyceryl backbone, processing of soybean oil will induce some degradation in a fraction of the triglyceride molecules to yield free fatty acid fragments. These compounds will not undergo base-catalyzed transesterification and must be esterified under acidic catalytic conditions.

Separation of the free fatty acids from the intact triglyceride molecules prior to conversion to esters is one of the challenges of processing soybean oil to biodiesel. Food grade soy oil can have very low free fatty acid content, less than 4%, in comparison with other oils, such as olive oil with up to 20%. However, lower quality feedstocks being considered for fuel production have higher free fatty acid content, with the highest concentration being present in waste oil that has usually been subjected to repeated heating cycles before being salvaged for biodiesel production. To process waste soybean oil, a combination of transesterification and esterification can be used, shown schematically in Figure 1. The waste oil passes through a centrifugal separator to remove water and suspended solids. The oil then moves to a tank of acid catalyst,  $\text{H}_2\text{SO}_4$ , and methanol. Upon esterification, three phases will form and separate: a rag layer containing acid, water, and methanol, a layer of unreacted oil, and the esterified products on the bottom of the tank. The lower two layers go through to the transesterification reactor, a reaction environment that does not degrade the already-formed methyl esters.

Triglyceride Chains	Normalized Mole Fraction	Ln (Linolenic) C18:3	L (Linoleic) C18:2	O (Oleic) C18:1	P (Palmitic) C16:0
LLLn	0.18	1	2	0	0
LLL	0.34	0	3	0	0
OLL	0.27	0	2	1	0
LLP	0.21	0	2	0	1
Mole fraction		0.083	0.751	0.083	0.083
Molecular weight, g	278	278	280	282	256

Table 1. Triglyceride Composition of Soybean Oil.

Recent expansion of biodiesel manufacture has resulted in increased interest among commercial enterprises to minimize the cost of feedstock materials and waste production and to maximize the efficiency of production. Hence, the technical issues limiting the feasibility of biodiesel production have received a lot of attention in the last decade. The next section discusses new approaches to converting soy oil to biodiesel highlighting the advantages that new technologies give over standard homogeneous base or acid-catalysis. Some ideas for improvement focus on gains in chemical kinetics or mass transfer, and others seek to reduce the amount of reagent methanol or simplify separations in pretreatment or posttreatment (preparation for sale). The next sections also present some of the drivers for advances in conversion technologies, along with recently published discoveries in making fuel from soybeans.

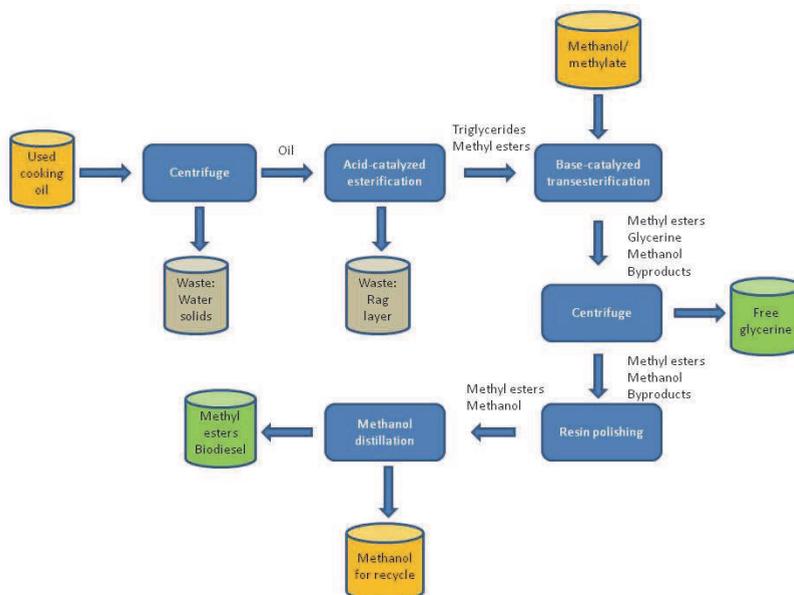


Fig. 1. A simplified flowsheet for the conversion of waste oil into methyl esters.

## 2. Advances in conversion technologies

Although homogeneous catalysts are used to promote the kinetics of the conversion of soybean oil to biodiesel, speeding up the process has inherent limitations. The reagent oil and alcohol, usually methanol, have limited miscibility, and so the reaction occurs primarily at the interface between the two liquid phases. Mass transport to the interface can be increased by rapidly mixing or forcing methanol into solution using higher pressures. Commercial processes are carried out at about 80°C, a temperature above the normal boiling point of methanol, to ensure conversion to the required ASTM specification. Even under pressurized conditions, the conversion takes at least half an hour in a batch reactor. At lower temperatures conversion typically take several hours. Several studies have investigated the use of supercritical methanol in the transesterification of soybean oil. Process intensification methods have been applied such as the use of rapid mixing and separation of products in a centrifugal contactor.

In addition to the issues with mass transfer, the kinetics of the three step transesterification can limit the overall conversion of the triglycerides to the esters. As the concentrations of intermediates increase, the rate of the back reactions can become significant with respect to the rates of the forward reactions. The online removal of glycerine to drive the process to completion has been attempted with some success; however, conversion to ASTM specification still takes minutes to complete. Addition of catalyst gives rise to saponification of the esters, resulting in phase separation and foaming, causing difficulties in processing. The reaction kinetics of transesterification has been modeled successfully with a three step forward and backward mechanism (Freedman, Butterfield et al. 1986; Nouredini & Zhu 1997). Although rate constants do vary with the type of oil and the processing conditions, the success with the model suggests that the constraints on reaction rate can be predicted and mitigated in a developing an optimized process flowsheet for soybean oil conversion to biodiesel.

Also problematic are multiple separation steps required during the conversion of soy oil to biodiesel. These include: pretreatment and removal of contaminants, separation of free-fatty acids from triglycerides, removal of free glycerine, washing to remove base catalyst, polishing of product in a resin bed, capture and recycle of unreacted methanol. In conventional processing, these steps can take several hours. However, the goal of some of the newer technologies being investigated in the laboratory is to minimize separation requirements.

A variety of new conversion technologies are being investigated to facilitate the conversion of soybean oil into biodiesel. Many of these ideas have been captured in recent reviews (i.e., (Lin, Cunshan et al. 2011), and a summary is given in the next section. Table 2 gives a synopsis of some of the new technologies, listing advantages and disadvantages for development on a commercial scale.

### 2.1 Advances in catalysis

#### 2.1.1 High temperature cracking and heterogeneous catalysis

Thermal cracking of triglycerides, as opposed to transesterification discussed earlier, has been carried out for over 100 years, with a recent focus on converting fats and oils to liquid fuels (Maher & Bressler 2007). The cracking process takes place at high temperatures, 300-500°C, and atmospheric pressure producing alkanes, alkenes, aromatics and carboxylic acids, that can be separated by distillation (Lima, Soares et al. 2004). The resulting mixture has a lower viscosity than the parent oil. Yields tend to be low in comparison with transesterification, although up to 77% conversion of soybean oil has been observed with the

use of a high quality, edible oil as the starting material. Although pyrolysis has been tested successfully on used cooking oil, fatty acid salts, and soaps, the low yields and the wide variety of chemicals produced in pyrolysis have made this process uneconomical. Difficulties with the pyrolytic method include the formation of char and cokes, as well as oxygenated compounds that need to be removed if the products are to be used as diesel substitutes. However, if the complex chemistry can be understood, and the decomposition pathways leading to aromatics and olefins as well as to more desirable alkanes identified, better control of reactor conditions to give desired products should be possible.

Processing Technology	Conditions & Reagents	Advantages	Disadvantages
<b>Homogeneous catalysis</b>	80°C. Mole ratio <sup>2</sup> ~6 (more needed for acid catalysis).	Used on commercial scale. Base catalysis has high yields	Batch process. Many separations needed. Corrosion.
<b>Heterogeneous catalysis</b>	160°C. Mole ratio ~12.	Flash separation of H <sub>2</sub> O & excess alcohol. Catalyst recyclable. H <sub>2</sub> O tolerant.	Small batch process. Lower yields <1 h. 80-90% yield at 3 h.
<b>Supercritical alcohol</b>	250°C. 200 bar. Mole ratio 30-80.	Complete conversion. Processing time < 1 h.	High mole ratio. Small scale only. High temperature. High pressure.
<b>Enzymatic catalysis</b>	50°C. 2 h reaction time. Mole ratio is 3.	Low temperature. Low mole ratio. Catalyst regeneration. Tolerant to H <sub>2</sub> O & free fatty acids.	Long reaction time. Rate depends on enzyme loading. Scaling difficult. Low yields. Expensive catalyst.
<b>Hydrodeoxygenation</b>	300-350°C. 45-70 bar H <sub>2</sub> . Mix with petroleum oil.	Diesel fraction linear alkanes produced. 100% conversion.	Long reaction time (hundreds of hours). High temperature. Mid pressure H <sub>2</sub> .
<b>Ultrasonic</b>	45°C. 1 h reaction time. Mole ratio is 6.	Low temperature. Continuous process. Scalable.	Longer reaction time/multiple passes (bound glycerine after one pass is 80-90 wt%).
<b>Centrifugal reactor/separator</b>	80°C. 2.6 bar. Mole ratio is 4.8.	90% conversion after 2 min. Staged approach to get ASTM spec.	Pressurized system.
<b>Metal foam</b>	100°C. 5 bar. Mole ratio is 10. 1 wt.% catalyst.	95% after 3.3 min. Low power (<1% conventional). 0.9 L/h throughput.	Pressurized system.

Table 2. Summary of soybean oil conversion technologies to biodiesel.

<sup>2</sup> Methanol-to-oil or alcohol-to-oil mole ratio unless otherwise specified.

Better selectivity may be achieved through the use of catalysts in the pyrolysis process (Maher & Bressler 2007). For instance, molecular sieve materials, being porous with high surface area, exhibit high catalytic reactivity. The tetrahedral structures of zeolites, or crystalline aluminosilicate  $\text{AlO}_4\text{-SiO}_4$  materials, show localized areas of high reactivity associated with the cations in the structure. Heterogeneous catalysis for pyrolysis of oils carried out at temperatures of 300-500°C over zeolites produces paraffins, olefins, carboxylic acids and aldehydes (Lima, Soares et al. 2004). Other studies using a protonated zeolite H-ZSM5 (85kPa He) have shown relatively more olefins and aromatics being produced from a variety of lipid starting materials and very little formation of oxygenated species. The reaction only generates a small amount of alkanes, and what is produced comes in the form of gases such as propane, and so is not appropriate for diesel fuel.

Metal catalysts have also been used for deoxygenation, Pt and Pd on activated carbon, at 300°C under nitrogen. Detailed analysis of the chemistry show that fragmentation of the triglyceride occurs more quickly than decarboxylation of the fatty acid chains. The fatty acid chains eventually form alkanes, with lighter hydrocarbons coming from  $\beta$ -fission at the double bonds. Lighter alkanes,  $\text{CO}_2$ , and CO come from the glycerol backbone. These studies demonstrate alkane production in the gasoline and diesel fraction range, with yields as high as 54% at 92% conversion for soybean oil (Morgan, Grubb et al. 2010).

A drawback to using catalyzed heterogeneous pyrolysis has been coking of the catalyst, requiring frequent cycles of oxidative regeneration (Milne, Evans et al. 1990). Fractionating batch reactors may allow the selective removal of alkanes, increasing their relative abundance, but yields are still relatively low (62 wt%) with high coke production (38 wt%) (Dandik & Aksoy 1999). Using mesoporous MCM-41 (1.93 nm pore size) as a catalyst showed lower gas production than H-ZSM5, with the best results being observed for palm oil, with 97.72% being converted overall and a yield of linear hydrocarbons C13-C17 in the diesel range of 42.52 wt.% (Twaiq, Zabidi et al. 2003). Palm oil differs from soybean oil with a higher fraction of shorter chain triglycerides, 50% C12 and 16% C14 and so these results may not relate directly to the conversion of soybean oil. In the same study, the authors show that experimentation with an oil of higher average molecular weight, in this case palm olein oil, showed a lower conversion and higher coke formation.

### 2.1.2 Low-temperature heterogeneous catalysis

Heterogeneous catalysis at low temperatures promises advantages over conventional processing in phase separation and avoidance of the use of strong caustic or acidic reagents. Some catalytic systems have proven to be more robust to fatty acids and to water than heterogeneous base catalysis (Zeng, Deng et al. 2009). The catalysts commonly used include transition metals and inorganic oxide systems that promote esterification and transesterification, besides the molecular sieves that are used in pyrolysis (discussed in Section 2.1.1).

A recent review gives details on supported solid metal oxides that have been used both for the transesterification and the esterification of oils to biodiesel (Zabeti, Daud et al. 2009). The transition metal oxides (alumina, tin, and zinc) form Lewis acids with the metal atoms acting as electron acceptors. Alkaline earth oxides (magnesium, calcium, and strontium) form Brønsted bases through the oxygen atoms in the structure. Because of the collocation of acidic and basic sites, the activity of the catalyst is often described in both of these terms (Yan, DiMaggio et al. 2010). In a series of steps, Figure 2, the metal atom coordinates with both the oxygen of the carbonyl group in the acylglyceride or fatty acid and the alcohol,

liberating a water molecule. The basic site can stabilize transfer of a proton from a fatty acid to water. The product ester forms within the supported complex or transition state, which decomposes regenerating the active metal oxide. Oxides such as alumina or silica can exhibit catalytic activity at acidic sites, dehydrating and decarboxylating fatty acids and triglycerides (Boz, Degirmenbasi et al. 2009). Acid-base catalysts can also be used in high temperature pyrolysis as well as for transesterification reactions.

Yields tend to be lower with heterogeneous catalysis in comparison with homogeneous catalysis (Section 1) because of reduced interfacial contact, not only between the oil and alcohol phases but also with the catalytic surfaces. To mitigate this limitation, methanol-to-oil ratios are usually high, 12 or greater; several wt% catalyst is often used; and reactions continue for a number of hours to drive the conversion to completion. Hence, studies are carried out in batch microreactors or autoclaves where extreme conditions can be controlled. Co-solvents have been used to improve the miscibility of the reagents (Yang & Xie 2007). Another way of improving reaction rate to get higher yields is to use high surface area catalysts and catalyst supports. For instance, nanoscale MgO has been used to achieve a 99% yield of methyl ester at 523°C and 24 MPa (Wang & Yang 2007). In autoclave studies of esterification at 160°C, a mass ratio of methanol: fatty acid: catalyst of 4: 10: 0.1 generated yields of up to 74% after only 1 h of residence time. The lowest yield, 32%, occurred in systems without the heterogeneous catalyst, with methanol: fatty acid: catalyst 4: 10: 0.0, showing that the catalyst had a significant effect on reaction rate (Mello, Pousa et al. 2011). The same group showed that higher yields could be achieved after 3 h of reaction time. They also demonstrated that the catalyst could be regenerated at least ten times using centrifugation and cleaning in solvent without an observable loss in performance.

Heterogeneous catalysis continues to generate much interest in the research community. Surface area and morphology appear to have a greater influence over catalyst activity than the chemistry of the catalysts. Although some of the conversions show promise, the extreme temperatures or pressures currently required for effective heterogeneous catalysis, as well as the relatively low yields in comparison with homogeneous catalysis, preclude them from being used on a large or commercial scale. However, many of the catalysts being considered appear quite robust, and although subject to coking and other deactivation processes, can be regenerated many times.

### 2.1.3 Enzymatic catalysis

Lipases, naturally occurring enzymes, have been used to catalyze the transesterification of triglycerides. The mechanism is thought to be a two step process, where the lipase reacts with one substrate to form a product and an intermediate enzyme, followed by reaction with another substrate to give a final product and the regenerated enzyme (Varma, Deshpande et al. 2010). The advantages of enzymatic processing are high yields of methyl esters, milder reaction conditions, high tolerance of water contamination, and easy separation of free glycerine. The lipase process can be done in a number of different solvents, including supercritical CO<sub>2</sub>. In the case of enzymatic catalysis, the loading of the enzyme has a profound effect on the initial rate of the reaction, and loadings of 5-10% w/w were found to be optimal. Enzymatic catalysis can be used for both esterification and transesterification, and a variety of oils and alcohols as feedstocks; however, processing conditions can be different depending on the starting material and desired product. Processing can take hours to reach equilibrium, typically achieved at when the reaction reaches about 50-70% conversion. Yields have been limited by inhibition of the catalyst by

the alcohol, although the enzyme can be regenerated by driving off the alcohol to regain its activity.

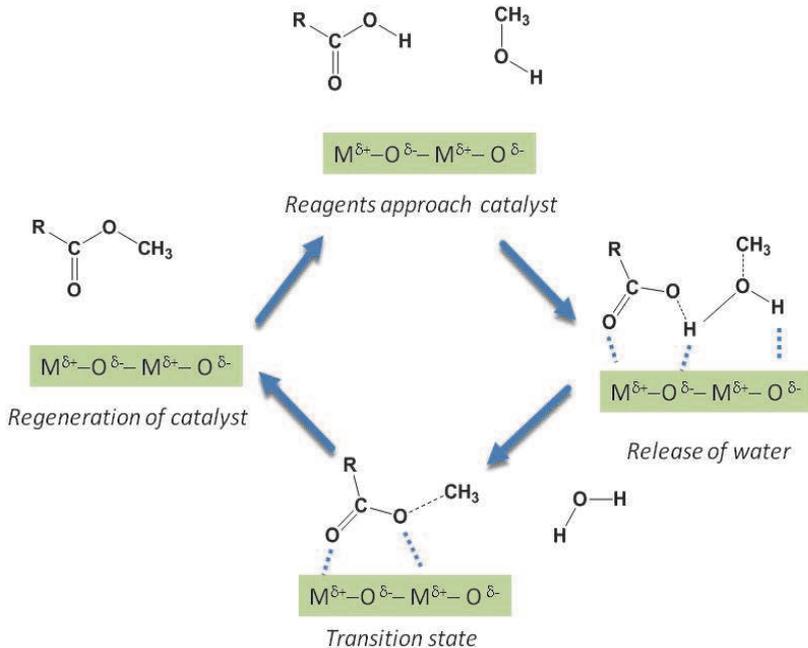


Fig. 2. Heterogeneous catalytic formation of a methyl ester from a fatty acid precursor.

## 2.2 Supercritical alcohols

A way of driving the transesterification reaction to completion without requiring catalyst is to perform the reaction under supercritical conditions. Many types of oils have been esterified in this way, including soy oil (Zhou, Wang et al. 2010). Both methanol and ethanol have been used as reagents (Rathore and Madras 2007). Pressures and temperatures are high for these processes, so that the conditions in the reactor exceed the critical point of the alcohols involved in the reaction. Pressures greater than 200 bar and temperatures exceeding 300°C are typical, although conversions of soybean oil have been successful at temperatures as low as 250°C. Because of the extreme conditions, these processes have only been demonstrated in the laboratory at bench scale. With a large excess of alcohol, the transesterification process can be described as a pseudo-first order reaction, and rate constants have been measured for a number of different alcohols reacting with a variety of oils (Varma, Deshpande et al. 2010). Rates of conversion in ethanol are greater than in methanol because of the greater miscibility of ethanol and the oil reagent. The rates also depend on the fatty acid content of the oil, being inversely proportional to the saturated fatty acid content.

### 2.3 Continuous and intensified processing

Conventional batch processing of soybean oil to biodiesel can take several hours, especially when post-conversion separation and polishing steps are included, see Figure 1. Each batch has to be tested against ASTM specifications before sale and a batch that has been compromised must be recycled back into the feed loop, adding cost. Properties of the fuel product can change because variations in the feedstock or changes in process condition. If implemented, a continuous process has the advantage of allowing online control of reagent flows, temperature and pressure conditions, to achieve good conversion, reducing the need for recycling of impaired product.

To achieve high conversion in a continuous process, however, issues such as the non-miscibility of reagents and mass transfer limitations in the transesterification process have to be overcome. Process intensification, an engineering concept that gained attention through investigations in the 1970s at the University of Newcastle (Stankiewicz & Moulijn 2002), is a way of enhancing mass transfer, thus reducing the capital cost of a chemical plant through a smaller plant size and reagent inventory and reducing operating costs through decreased energy consumption and feedstock required per unit mass of the product. Centrifugal phase contact and separation is an example of an intensified technique that enhances mass transfer at high throughput and minimizes the inventory of solvents (Tsouris & Porcelli 2003). Another example is to use bubble formation to increase the interfacial area of immiscible fluids, which can be induced by introducing energy to the system through acoustic coupling (Cintas, Mantegna et al. 2010).

Process intensification methodology has been adapted to enhance the pretreatment of biodiesel feedstocks, the conversion reactions, or the posttreatment separation of reaction products. A cavitation reactor was used in the process intensification of the homogeneous acid ( $\text{H}_2\text{SO}_4$ ) catalyzed esterification of simulant fatty acids (Kelkar, Gogate et al. 2008). High throughput ultrasonic irradiation at 21.5 kHz coupled with a stirred tank was used to make a fine emulsion of oil and methanol, thereby increasing the interfacial area. The reactor achieved a yield of >80% methyl esters from soybean oil (Cintas, Mantegna et al. 2010). In this apparatus, temperatures were kept low,  $\sim 45^\circ\text{C}$ , to prevent boiling of methanol in the microwave reactor. A sonochemical reactor has also been used to enhance the base-catalyzed transesterification of lightly used cooking oil as well as food grade vegetable oil (Hingu, Gogate et al. 2010).

Centrifugal mixing has been applied to biodiesel production (Peterson, Cook et al. 2001), because of its ease of operation, rapid attainment of steady state, high mass transfer, phase separation efficiencies, and compact size (Leonard, Bernstein et al. 1980). The high shear force and turbulent mixing achieved in a contactor minimize the effect of diffusion on the reaction rate of transesterification, pushing it to be limited only by the reaction kinetics. The contactor has been used as a low-throughput homogenizer, employing very low flow rates to increase residence times to tens of minutes (Kraai, van Zwol et al. 2008; Kraai, Schuur et al. 2009).

At ORNL, we have combined the reaction of oil and methoxide with the online separation of biodiesel and glycerol into one processing step, using a modified centrifugal contactor. Two distinct phases enter the reactor (reagents: methanol and base catalyst; and vegetable oil), and two distinct phases leave the reactor/separator (products: glycerol and methyl ester), thus demonstrating process intensification in high-throughput biofuel production. The ORNL reactor separator was modified from a commercial unit, Figure 3a, to increase the residence time from a few seconds to a few minutes by achieving hold-up in the mixing

zone, Figure 3b. (Birdwell, Jennings et al. 2009). In the ORNL tests, base-catalyzed transesterification of soybean oil was carried out at continuous flow conditions at 60°C and in static pressurized tests at 80°C (McFarlane, Tsouris et al. 2010).

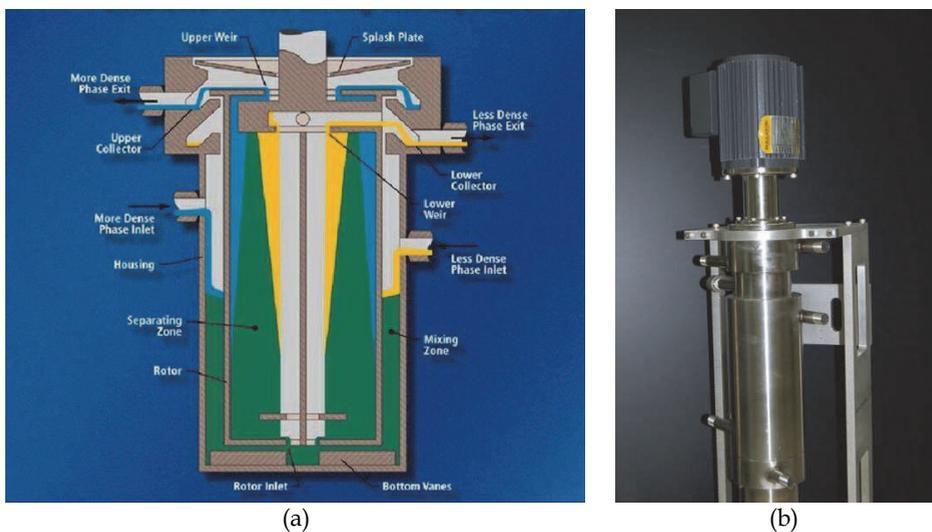


Fig. 3. Reactor-separator housing: a) commercial unit schematic, b) modified contactor housing.

Besides bubble formation and stirring, another way of achieving high turbulence and good mass transfer for the production of biodiesel is through the use of reactors involving tortuous flow pathways. These concepts were first tested on microreactors, involving zigzag channels (Wen, Yu et al. 2009). Although high conversions were achieved, 99.5% at 28s residence time, scaling the reactor up from microliter  $s^{-1}$  flow rates has not been possible. More recently, turbulence has been achieved by passing the reagents through porous metal foam, which can be made to have a high pore density (50 pores per inch) and a relatively low pressure drop (0.6 MPa). At 100°C and with a methanol-to-oil mole ratio of 6, a conversion of 90.5% was observed (Yu, Wen et al. 2010). With the foam, the arithmetic mean drop size of the disperse phase was about 3  $\mu m$ . By balancing the effect of smaller, high surface area bubbles at high flow rates, with the lower residence time, conversions were pushed to 95 mol% with a flow rate of 0.9 L  $h^{-1}$ . While high for a microreactor, this flow rate is much lower than for competing continuous technologies.

In all continuous processes, the conversion of soybean oil to esters is limited by residence time in the reactor. Producers and investigators have focused on the kinetics of transesterification to determine if conversions to methyl ester are limited by mass transfer effects or by slow kinetics (Darnoko & Cheryan 2000; Karmee, Mahesh et al. 2004). In the transesterification reaction, mass transfer limitations early in the process become superseded by kinetic limitations when trying to achieve high yields of methyl esters. In the case of the Oak Ridge experiments, although 90% conversion was achieved in 2 min, a 22 min residence time at 80°C was needed to achieve ASTM specification grade fuel, ~98% conversion, Figure 4. Hence, in both the centrifugal processing and the ultrasonic reaction, multiple stages were found to shorten reaction time and reduce energy consumption. The online

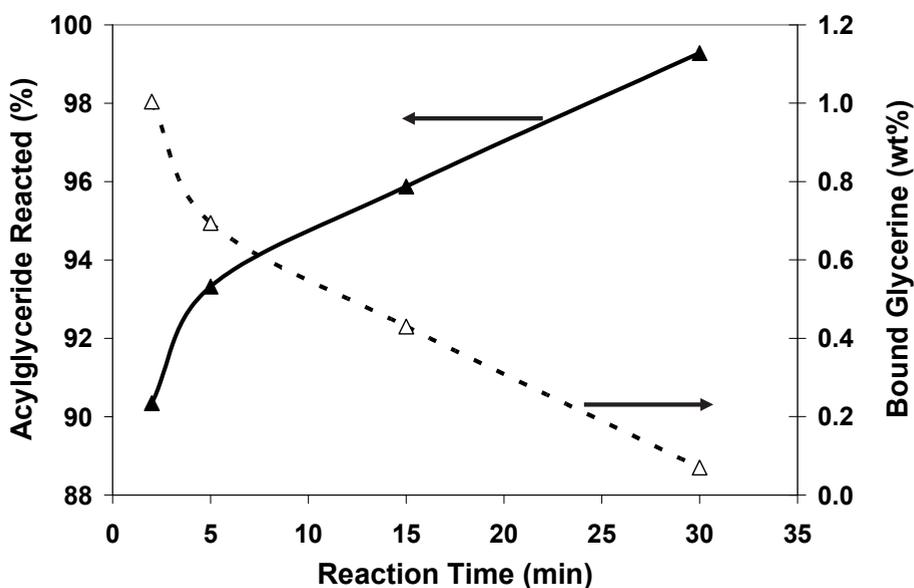


Fig. 4. Yield of batch transesterification reaction in continuous contactor in terms of the weight percent of triglyceride reacted ( $\blacktriangle$ ) and remaining total bound glycerine ( $\Delta$ ) as a function of reaction time (80°C, above ambient pressure to 2.6 bar, 3600 rpm rotor speed). The arrows indicate the conversion goal of <0.24 wt% bound glycerine, or 97.8% conversion of acylglyceride.

separation of free glycerine removes a sink for the base catalyst (Cintas, Mantegna et al. 2010), as well as reduces back reactions to form bound glycerine species (McFarlane, Tsouris et al. 2010). The accelerated reaction achieved with online separation also prevents thermal degradation of the methyl esters, arising from beta scission adjacent to the carbonyl group and cleavage of the unsaturated bonds in the fatty acid chains (Nawar & Dubravcic 1968; Osmont, Catoire et al. 2010).

### 3. Generation of fungible fuels from plant oils and new technologies for de-oxygenation

Even after esterification, the product biodiesel can be substituted directly for standard diesel fuel only to a limited percentage and is normally restricted from portions of the United States common carrier distribution system<sup>3</sup>. Although biodiesel has a similar cetane number to hexadecane, the higher oxygen content causes changes in the combustion profile and can enhance corrosion of engine seals (Haseeb, Fazal et al. 2011). The higher oxygen content also means that the heating value of methyl esters is slightly lower than standard diesel, although the reduction is not nearly as large as is when comparing ethanol to gasoline. The

<sup>3</sup> ASTM specifications allow 5 vol.% fatty acid methyl esters (FAME) in commercial diesel fuel.

lower volatility and higher oxygen content of biodiesel change the injection profile in a compression engine, and hence the ignition timing and production of pollutants, for instance decreasing soot and increasing the  $\text{NO}_x$  in the exhaust (Ra, Rietz et al. 2008; Toulson, Allen et al. 2011). This active area of study has an impact on high efficiency clean combustion engines, the vanguard of advanced diesel engine design. In most standard vehicles, biodiesel concentrations are limited to a blend of 20% to mitigate the effects of its physical properties being different from those of standard diesel fuel (Mushrush, Willauer et al. 2009), such as poor cold flow. In addition, biodiesel has a limited shelf life and can form precipitates and go rancid in storage, causing problems in distribution.

One method of producing deoxygenated products from soybean oil is to use a high temperature (350-450°C) hydrogenation process rather than transesterification to make fuels. This hydroprocessing, carried out over supported catalysts, is different than the pyrolytic schemes described in some detail in Section 2.1.1 because hydrogen is introduced directly into the reactor. Heavier paraffinic fragments are produced rather than the small gaseous alkanes made in pyrolysis. The process, as applied to triglycerides, has been reviewed by Donnis and colleagues (Donnis, Egeberg et al. 2009). Hydrotreating experiments on triglycerides have used the same conventional catalysts used in hydroprocessing oil, such as sulfided NiMo or CoMo on alumina under relatively low pressures of  $\text{H}_2\text{S}/\text{H}_2$  mixtures (Huber, O'Connor et al. 2007). The process includes several chemical steps to give alkanes as a final product, including: hydrogenation of  $\text{C}=\text{C}$  bonds; decarboxylation (removal of  $\text{CO}_2$ ); decarbonylation (removal of  $\text{CO}$ ); and dehydration (hydrodeoxygenation (HDO) to convert  $\text{COOH}$  to  $\text{H}_2\text{O}$ ). The glycerin backbone may react to form methane or propane (Donnis, Egeberg et al. 2009). By carefully controlling temperature and reaction time the yield of the paraffinic diesel-fraction, or straight chain  $\text{C}_{15}\text{-C}_{18}$ , can be maximized. Although some studies show that catalyzed hydroprocessing over nickel generates too many aromatics and cyclic compounds, tailoring of HDO products by additional isomerization steps has been suggested to produce branched alkanes (Jakkula, Niemi et al. 2004). This would give a biorefinery the ability to produce the desired fuel properties for vehicular use without the need for blending, giving a product similar to Fischer-Tropsch diesel fuel from natural gas.

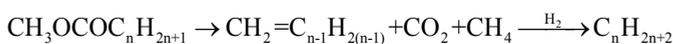
Huber and colleagues have also shown that the bio-derived oils can be hydrotreated along with petroleum oils, suggesting that a processing can take place within an existing refinery to lower the capital cost. Issues with hydroprocessing vegetable oils rather than petroleum include: the high oxygen content of biomass can increase heat load in the reactor and cause leaching of sulfur from the catalyst; water and  $\text{CO}_2$  generated during the hydrotreatment can reduce catalyst lifetime and must be removed from the product; and also the large triglyceride molecules can clog catalysts with pore sizes of less than 2 nm (Tiwari, Rana et al. 2011). Mesoporous molecular sieves, such as MCM-41, or alumina can have the advantage of a high surface area and activity, but also have much larger pore diameters than zeolites (Kubicka, Simacek et al. 2009), and so may be useful in a combined bio-petro refinery.

Another route to achieving a hydrocarbon rich fuel from soybean oil is through deoxygenation of the esters after the transesterification process has taken place. In this case the biodiesel produced from soybean oil is further reacted to form a hydrocarbon fuel. The processing involves deoxygenation to remove the ester moiety from the hydrocarbon chain. With this step, the product becomes completely miscible with standard diesel fuel and can be introduced at any step in the supply chain, either at the refinery or at the filling station. Note that if blending is done at the terminal or filling station, the product has to meet

completely ASTM specifications. Some of these processes involve hydrogen and some do not.

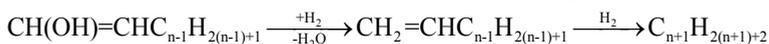
The hydrogenation of methyl octanoate, as a simulant for methyl esters from biodiesel, has been carried out over an N-ZSM5 zeolite catalyst under atmospheric pressure  $H_2$  (Danuthai, Jongpatiwut et al. 2009). The experiments were run over a few hours at temperatures up to  $500^\circ C$ , and showed 99.7% conversion of the ester to C1-C7 alkanes - a third comprising ethane, and small aromatics (C6-C9). Residual oxygenated species comprised only 2.8%. The group also found that the aromatic fraction increased with the time in the reactor, and that  $H_2O$  promoted the catalytic activity of the zeolite by enhancing production of an acid byproduct, obviously undesirable as a fuel component. Tests with methyl octanoate, a smaller molecule than methyl esters derived from soybean oil, showed conversion to alkanes and aromatics through formation of a high molecular weight ketone intermediate. The patent literature suggests that similar results have been achieved with longer fatty acid chain methyl esters from soybean and other oils (Craig 1991). Reaction 4 shows the overall conversion process of a methylester to a linear alkane by hydrodeoxygenation: step A) removing the oxygen as  $CO_2$  or methanol followed by formation of the enol, and step B) involving hydrogenation and dehydration of the enol to the linear alkane (Donnis, Egeberg et al. 2009).

A)



(4)

B)



As discussed in Section 2.1.1, non-hydrogenated direct catalytic cracking of triglycerides can lead to products with greater oxygen content than desirable for fuels. Better control of the cracking process can be engineered when starting with an esterified feedstock. A recent example is the use of supported platinum and bimetallic platinum-tin catalysts in the deoxygenation of methyl octanoate, methyl dodecanate, and soybean oil by reactive distillation at  $320$  to  $350^\circ C$ . By manipulating the residence time and the catalyst properties, selectivity for paraffins of 80% was achieved. Overall yields were low, suggesting this process requires more investigation before commercialization (Do, Chiappero et al. 2009; Chiappero, Do et al. 2011).

#### 4. Feasibility of using plant oils for fuels in comparison with petroleum, ethanol, and lignocellulosic feedstocks

The use of soybean oil in production of biodiesel has been primarily limited by economic factors, in particular the cost of the feedstock. Less expensive fuel can be made from degraded starting material such as waste oil. Energy crop alternatives to seed oils have also

been proposed (Vinokurov, Barkov et al. 2010). However, the processing of feedstock with higher free fatty acid content adds complexity to the manufacturing process, particularly because of the variability in composition and treatment prior to conversion. The solution to tightening of petroleum supply will likely involve liquid fuel generation from a variety of sources. As should have been apparent from the previous discussion, the processing of biomass-derived oils into burnable esters depends on the chemical composition of the feedstock: the relative concentration of free fatty acids, the saturated versus unsaturated fatty acid chains, impurities and water content.

An additional cost is associated with the alcohol used to convert the seed oil to biodiesel, typically used in amounts well above stoichiometric to push the reaction to completion. An analysis was recently done at ORNL where the cost of a three stage biodiesel manufacturing process was assessed based on the reactor-separator reactor discussed in Section 2.3 (Ashby & McFarlane 2010). In order to optimize the process, environmental conditions such as temperature, pressure, and the starting proportion of methanol-to-oil were all varied individually. Each of these aspects of the production affected the residence time and the fraction of soybean oil converted during the reaction, hence the economics of the process. The analysis gave the projected capital cost for a new plant and its projected profit in the first five years. These analyses revealed that reactions run at higher temperatures needed less time to convert a larger fraction of triglyceride. Reactions with a greater proportion of methanol-to-oil had a higher yield at a residence time of 600s than those with a lower ratio. Figure 5 shows the effects of adding additional methanol at various stages of a five stage process.

An economic analysis shows that production of biodiesel should be more profitable in a three contactor series than a single reactor given similar process conditions, i.e., temperature and ratio of methanol-to-oil, in spite of the costs associated with the reactor and pumps for each additional stage. In the long term, the feedstock soybean oil comprised the highest fraction of the operating expenses, ranging from 70-80% of the total. The cost of the alcohol was also found to be significant, but could be minimized through recycling, thereby also reducing the carbon footprint of the process. In this analysis, the production of biodiesel from soybean oil could only become profitable if the product could be sold at about 1.5 times the cost of the soybean oil feedstock (assuming a 300,000 gal/year operation amortized over 5 years). Based on simulation of the chemical kinetics of soybean oil transesterification, the highest yield of methyl esters in the shortest time arose from using three reactor-separators in series, each with a 200s residence time, recycling of all excess methanol, a 4.5-to-1 initial proportion of methanol-to-oil, and an operating temperature of 100°C. Similar analyses have been done for other reactor configurations, feedstocks, alcohols, and catalysts, to assess the viability of these process designs for commercial production of biodiesel (Peterson, Cook et al. 2001).

In the case of soybean utilization, the feedstock costs appear to dominate the potential use of biomass conversion to supplant petroleum-derived diesel in any of the reactor configurations being considered (Lin, Cunshan et al. 2011). However, the economics of biodiesel production can be improved if value added products can be developed from the byproduct glycerine. Janaun and Ellis give many of these in their review: catalytic conversion to oxidized products such as propylene glycol; biological conversion to lipids and citric acid; fuel oxygenates; gasification to H<sub>2</sub> and syngas; remediation of acid mine drainage; and in agriculture as animal feed (Janaun & Ellis 2010).

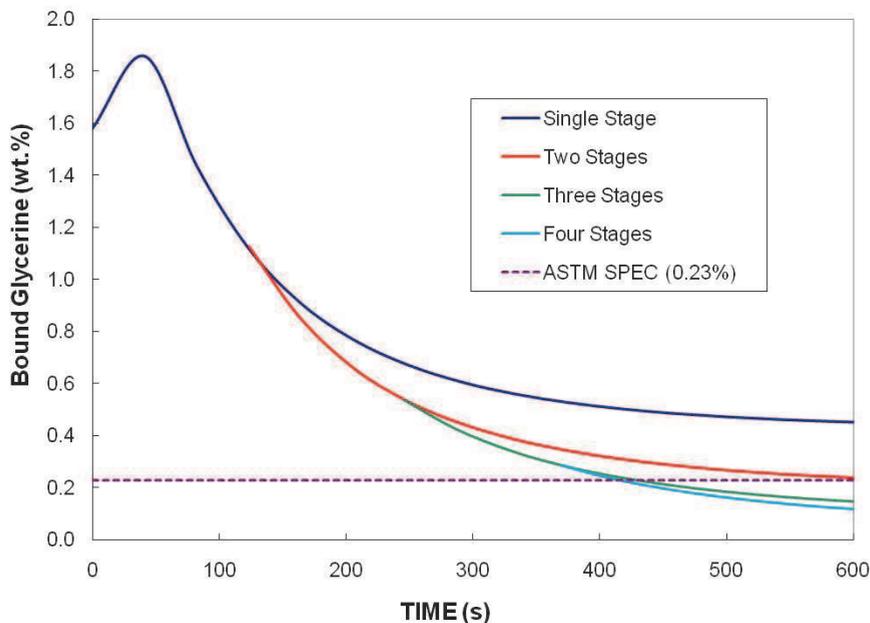


Fig. 5. Bound glycerine content as a function of time for various options of methanol addition, at 80°C: Single stage involves no additional input of methanol over 600s reaction time; Two stages involves adding 10% original methanol charge at 2<sup>nd</sup> stage; Three stages involves adding an extra 5% original methanol charge at 3<sup>rd</sup> stage; Four stages has no additional methanol as the effect is minimal by this point.

Another aspect worth consideration is that unless specifically designed to do so, compression engines are not constructed to handle the higher oxygen content of biofuels such as biodiesel or ethanol. Hence, many alternative fuels under consideration are blended to give the properties needed for engine performance and fuel stability, 10% ethanol in gasoline being a common example. However, fuel from different sources may not be compatible. Biodiesel, with its high oxygen content, mixes well with standard diesel, but not with purely paraffinic Fischer-Tropsch fuel. The aromatics in standard diesel solubilize the olefinic chains and electron-rich esters, whereas tertiary carbons in the Fischer-Tropsch paraffins appear to form stable hydroperoxides with degradation products in the biodiesel (Mushrush, Willauer et al. 2009). If the biodiesel contains unreacted free-fatty acids, phase separation and precipitates are likely to form. One possibility is to hydrogenate the biodiesel to create a fully hydrocarbon fuel, as discussed earlier in Section 3. Another is to exploit the properties of other biomass-derived fuels to produce a blend with properties that meet the requirements for compression ignition engines. For instance, lignin has the potential to become a biofuel feedstock can be broken down into appropriately sized aromatic fragments, which can be used as additives to diesel fuel or to biodiesel methyl esters (Gluckstein, Hu et al. 2010). The properties of the blend will have the high cetane number and the high lubricity of the biodiesel methyl esters, but with the reduced viscosity and low

cloud point of the aromatics. Hence, while a pure biofuel may have some undesirable characteristics, mixtures of alternative fuels may be compatible with standard diesel engines. An assessment of mixtures of diesel compatible formulations has been performed by the Fuels for Advanced Combustion Engines (FACE) Project and target properties are presented in Table 3. The average properties of marketed diesel fuel are shown in brackets (Gallant, Franz et al. 2009).

Property	Range for FACE project	Standard Diesel Fuel	Soybean Methyl Esters
Cetane number	30-55	43-51	51
Aromatics (%)	20-45	32	0
T90 Distillation (°C)	270-340	320	Not applicable
Specific gravity (g cm <sup>-3</sup> )	0.803-0.869	0.82-0.86	0.884
Heat of combustion (kJ/kg)	7790-7980	7850	Reduced by 9-13%
Kinematic viscosity (mm <sup>2</sup> s <sup>-1</sup> )	1.319-3.218	1.90-4.1	4.08
Cloud Point (°C)	-19.5--55.5	-18--30	-0.5
Flash Point (°C)	53-74	55	131
Pour point (°C)		-25	-4
Constraints	< 15 ppm sulfur, <4% olefins Smooth distillation curve		

Table 3. Fuel Formulation Property Targets for Compression Ignition Engines.

Biofuel production in the US and Brazil is dominated by ethanol, where as biodiesel has greater importance in Europe (Rusco & Walls 2009). In some respects the issues with ethanol and biodiesel are similar, competition for agricultural resources with food, oxygen content and lower heating value, and distributed production (Kalnes, Marker et al. 2007). Varying fuel standards can further complicate distribution, leading to lower pipeline capacity and increased storage requirements. For instance, ethanol, even blended with gasoline, currently is not transported through pipelines because of its high affinity for water resulting in corrosiveness and phase separation. However, ethanol is a simple molecule that has the same composition no matter the source, and its impact on petroleum refining can be assessed on a large scale. This is not the case for plant-based biodiesels, from which a variety of fuels can be produced depending on the plant variety and processing conditions. Depending on the regulatory environment and governing standards, this may further break up the markets for biodiesel production and distribution. For example, southern regions will better be able to tolerate higher cloud points than northern, both for pipeline, truck and rail transport, as well as for combustion in passenger vehicles. The cost of the adoption of biofuels needs to be assessed along with benefits, such as reduction in greenhouse gas emissions, energy security, or support of US agriculture (Rusco & Walls 2008).

## 5. Conclusions

Although the price of diesel fuel has increased, economical production of biodiesel is a challenge because of (1) the increasing price of soybean oil feedstocks and reagent methanol, (2) a distributed supply of feedstocks that reduces the potential for economies of scale, (3)

processing conditions that include pressures and temperatures above ambient, and (4) multiple processing steps needed to reduce contaminant levels to ASTM specification D6751 limits (Vasudevan & Briggs 2008). Much of the cost of biodiesel production is related to the conversion of the oil to the methyl ester and so there has been an emphasis to research improved methods of converting soybean oil to biodiesel. However, most of these studies have taken place at the bench scale, and have not demonstrated a marked improvement in yield or reduced oil-to-methanol ratio in comparison with standard base-catalyzed transesterification.

One aspect that has a short term chance of implementation is the improvement of the conversion process by the use of a continuous rather than batch process, with energy savings generated by combined reaction and separation, online analysis, and reagent methanol added by titration as needed to produce ASTM specification grade fuel. By adapting process intensification methods, recycled sources of soybean oil may also be used for diesel production, taking advantage of a lower priced feedstock material.

Even if the economics of production are feasible, biodiesel distribution is complicated by thermal stability and degradation over time, and the physical properties of methyl esters make them undesirable for standard compression ignition engines in concentrations greater than 20% in a blend with diesel fuel. Generation of truly fungible fuel from biomass is now being investigated through a variety of routes. However, it is too early to judge which will become the most viable.

The promise of soybean-generated biodiesel is that of a truly fungible, thermodynamically and economically viable technology providing a biomass replacement for a petroleum product. The use of biodiesel has the potential to reduce the amount of CO<sub>2</sub> released to the atmosphere by the transportation sector; to provide an additional source of liquid fuel that can be produced in small distributed operations; and to allow the processing of waste oil-to-energy that can result in enhanced lifecycle efficiencies as well as reduced environmental footprint.

## 6. Acknowledgments

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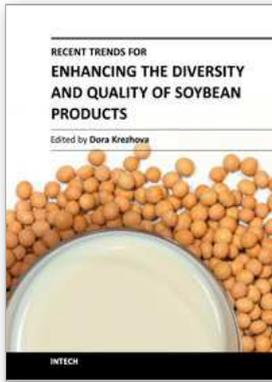
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## **Recent Trends for Enhancing the Diversity and Quality of Soybean Products**

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This book presents new aspects and technologies for the applicability of soybean and soybean products in industry (human food, livestock feed, oil and biodiesel production, textile, medicine) as well as for future uses of some soybean sub-products. The contributions are organized in two sections considering soybean in aspects of food, nutrition and health and modern processing technologies. Each of the sections covers a wide range of topics. The authors are from many countries all over the world and this clearly shows that the soybean research and applications are of global significance.

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