

**Yield Characteristics of Biodiesel Produced from Chicken
Fat-Tall Oil Blended Feedstocks**

**Completion Report
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Abstract

The primary objective of this study was to investigate the conversion of chicken fat and tall oil, both individually and in a blend, into biodiesel. The conventional base-catalyzed method of biodiesel production has shown to be inappropriate for the conversion of high free fatty acid-containing feedstocks such as tall oil, due to the undesired saponification reaction that takes place. Likewise, the acid-catalyzed method of biodiesel production has been shown to be inappropriate for the conversion of triglyceride-containing feedstocks, such as chicken fat, due to the long reaction times and large excess of methanol required. Therefore, an alternate reaction pathway was investigated for these two very different feedstocks. Supercritical methanol treatment, which requires no separate catalyst, was the method chosen.

Following the development of proper protocol, both chicken fat and tall oil fatty acids were reacted in supercritical methanol to produce biodiesel under a matrix of temperatures and methanol to feedstock ratios. Results indicate that the chicken fat and tall oil fatty acids can be converted successfully in a single step with yields in excess of 89% (out of 91% max) and 94% respectively. The optimum temperature and excess methanol was determined, and the results suggest the use of a two step process involving the initial hydrolysis of triglyceride-containing feeds followed by the supercritical esterification of the resulting/existing free fatty acids. The results of one such test proved to be satisfactory, and are reported herein. Furthermore, crude tall oil was also tested in the system to investigate its viability as a biodiesel feedstock with limited success.

Cold flow properties, such as viscosity and cloud point, are reported for the resultant fuels. The viscosities of all of the fuels exceeded the ASTM D6751 acceptable specifications for biodiesel; therefore blending with other biodiesel fuels such as methyl soyate would be required for widespread use of the fuels produced under the conditions reported herein as commercial biodiesel.

Introduction

Biodiesel is a non-petroleum based alternative diesel fuel that consists of alkyl esters derived from renewable feedstocks such as plant oils or animal fats. These feedstocks commonly contain triglycerides and free fatty acids, which can undergo transesterification or esterification reactions (respectively) to produce the alkyl esters that make up biodiesel. One such alkyl ester, methyl oleate, is shown in Figure 1.

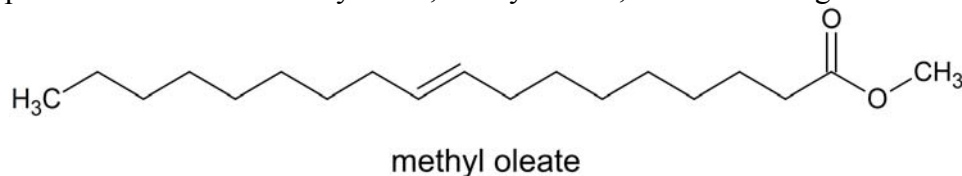


Figure 1. Example of a methyl ester found in biodiesel

Biodiesel holds many advantages over conventional petroleum diesel (“diesel”). Some of the more publicized reasons include the fact that biodiesel is renewable, biodegradable, and locally produced while offering a low toxicity, high cetane index, and a carbon-neutral fuel source. Some other advantages include superior lubricant and solvent properties, lower emissions of harmful chemicals, and the ease of storage, transportation, and adaptation into current equipment and infrastructure.

Biodiesel can be formed in a matter of months from feedstocks produced locally. Not only does this support a more sustainable energy infrastructure, it also lessens the need for foreign imports of oil while creating labor and market opportunities for domestic crops. A wide range of feedstocks can be used in the production of biodiesel including, but not limited to virgin or refined tree and vegetable oils, waste fryer oil, animal fats, pond algae, or even a combination of feeds. It is the ability to adapt the production process to locally available raw materials on an intermittent basis that helps make biodiesel an attractive alternative to petroleum diesel⁵.

From an environmental and safety standpoint, biodegradability and toxicity are important properties of a fuel. Peterson and Möller¹ tested the biodegradability of diesel fuel, biodiesel fuel from soybean and rapeseed oils, as well as various diesel/biodiesel blends in aquatic and soil environments. Over a period of a month, they observed the aquatic biodegradation of biodiesel and diesel/biodiesel blends to be 77 and 86% respectively. For pure petroleum diesel, it was only 18.2%, showing that biodiesel degrades approximately 4 times as fast as conventional diesel in aquatic environments. Interestingly, co-metabolism was observed in the biodegradation of the diesel/biodiesel blends, as apparent by the data. Over the same length of time, the average disappearance of the fuels from soil samples was found to be ~88% for the biodiesel fuels and 52% for petroleum diesel. In fact, biodiesel was found to be just as biodegradable as simple sugar. Toxicology tests from the same study showed that biodiesel is not only considerably less toxic than diesel fuel (LC₅₀ of 587.15 mg/L for 48 hours), but up to 89 times less toxic than table salt, making it a safer and more environmentally friendly alternative fuel.

The cetane index is an important property of a diesel fuel which is a measure of the tendency for it to auto ignite with respect to a reference fuel, cetane (index of 100). Encinar et al.² compared the cetane indices of several biodiesel fuels from various feedstocks to that of No. 2 diesel fuel. They found that the cetane index for biodiesel, which ranged from 47 to 52 depending on the feedstock used, was greater than that of the diesel fuel. Canakci and Van Gerpen³ as well as Knothe⁴ report similar conclusions. This slightly higher cetane index signifies improved combustion control in the diesel engine, which increases performance when using biodiesel.

Since much of the carbon found in the oils and fats used to create the fuel originated from CO₂ in the atmosphere, biodiesel is considered to contribute much less to global warming than conventional diesel. Plants that are grown to make biodiesel, such as soybeans, naturally balance a good portion of the CO₂ that is released during fuel combustion. In a study by the National Renewable Energy Laboratory (NREL), a life-cycle analysis of biodiesel showed that overall CO₂ emissions were reduced by 78% when compared to petro-diesel⁵. These findings signify sustainability in biodiesel use with the potential to slow global warming caused by greenhouse gas emissions.

One property of biodiesel that has gained a lot of attention is its ability as a lubricant. Diesel engine components such as fuel injectors and some types of fuel pumps rely on the fuel itself for lubrication. Environmental regulations that forced the removal of sulfur from diesel fuels down to 500 ppm (low-sulfur diesel) were followed by reports of these engine components failing in the United States and Europe, most likely due to the low lubricity of these cleaner fuels⁶. Interestingly, it has been shown that it is not the removal of the sulfur compounds that causes this decrease in lubricity, but rather the co-current removal of oxygen and nitrogen containing compounds in this process⁷. These harmful effects are expected to be magnified with the recent EPA-mandated use of ultra low-sulfur diesel (< 15 ppm sulfur) in June of 2006. This fuel is expected to have a much lower lubricity than even the low-sulfur type. It has been reported by many that biodiesel has a much higher lubricity than conventional diesel, especially the low- and ultra low-sulfur diesel fuels^{8,9}. The presence of oxygen moieties in the biodiesel, found to be as high as 10% by mass in some fuels, has been suggested to impart lubricity to the fuel. The addition of biodiesel to the lower sulfur fuels at volumetric blends even less than 1% has been reported to restore the recommended lubricity of the fuel. These findings show that the use of biodiesel can extend engine life not only as a substitute fuel, but also as a fuel additive.

The alkyl esters found in biodiesel have also been shown to have exceptional solvent properties. Potential applications include industrial cleaning operations such as oil-spill remediation, resin cleaning, and degreasing. Du et al. investigated the solvent power of various biodiesel fuels derived from different feedstocks¹⁰. High solvent powers were obtained, and were found to be adjustable based on the feedstocks used. When switched over to biodiesel, some diesel engines have been found to experience plugging of fuel filters or injectors, most likely caused by petroleum deposits that were left by the use of conventional diesel. It was found that the biodiesel dissolved these deposits, which were further caught in the peripheral equipment, causing these malfunctions. While the removal of carbonaceous deposits is an invaluable service that can greatly increase the life of the engine, care should be taken to slowly transition (by

blending) from diesel to biodiesel to avoid these side effects¹¹. From an environmental standpoint, the combination of biodegradability, low toxicity, and solvent capabilities make biodiesel a very eco-friendly fuel and industrial solvent, adding to the list of accolades.

Biodiesel use has also been reported to reduce the emissions of several harmful chemicals with respect to diesel, including carbon monoxide, carbon dioxide, sulfur dioxide, particulate matter, and other unburned hydrocarbons¹². A study by Tat et al. showed that with respect to conventional diesel, there was a reduction of up to 33% in CO, 53% in unburned hydrocarbons, and significant reductions in smoke emissions when substituted with biodiesel¹³. While this study showed mixed results with nitrous oxide emissions, many have reported that these emissions are slightly increased when biodiesel is used, but the use of proper additives can eliminate this issue. The results from these studies are very promising for reducing emissions of greenhouse gases and other harmful chemicals.

Due to their many similar properties, the transition from conventional diesel to biodiesel could be almost seamless. Many tests have concluded that the diesel engine can operate on pure biodiesel with little modification, if any. Dalai and Kulkarni¹⁴ report the testing of various pure or diesel-blended alkyl esters with respect to engine performance. The only deterioration of performance or equipment was reported with older engine models that use rubber gaskets and seals. The solvent ability of biodiesel causes degradation of the rubber allowing fuel leaks to occur. However, these seals can be easily updated to more resistant materials that the newer engines utilize. The alkyl ester fuel gave combustion efficiencies of approximately 66% while conventional diesel gave only 56%, signifying an increase in engine performance when using biodiesel. While in some cases, the ester fuels showed larger fuel consumptions than conventional diesel (most likely due to the slightly lower energy value of the former), it is believed that the increase in combustion efficiency should help offset this issue. Furthermore, biodiesel has been shown to have a higher flash-point temperature, making the storage and transportation of the fuel easier and safer¹⁵. Most importantly, the infrastructure that is currently in place for fuel collection and delivery would not be affected by the transition. Proposed energy regimes such as the use of compressed natural gas or the ever-popular hydrogen fuel require extensive changes to the fuel infrastructure already in place, inhibiting their use. On the contrary, many biodiesel fuel pumps have actually appeared at gas stations around the U.S. with biodiesel-blended fuel.

While biodiesel does have some disadvantages, such as a lower energy density and possibly higher NO_x emissions, they are overshadowed by the many benefits. Biodiesel provides an effective, sustainable-use fuel with many desirable properties. While estimates have shown that biodiesel alone cannot displace petroleum diesel consumption in the U.S., any displacement is significant. The only major disadvantage is the production cost, driven high by feedstock prices and availability. By finding other, or possibly less refined materials that are suitable for the process, biodiesel production costs could be decreased to compete with conventional diesel. Currently, most of the global biodiesel is produced from refined vegetable oils that contain mostly triglycerides with limited free fatty acids. These refined oils, such as soybean and rapeseed oil, are expensive, and generally account for 60-80% of the total cost of biodiesel^{15,16}. Due to

these high feedstock prices, without government-granted tax breaks, biodiesel is not currently cost-competitive with petro-diesel. More recently, some less refined and less expensive feedstocks have been tested for use in biodiesel production so that it may better compete with conventional diesel. It is the purpose of this study to investigate two such alternative feedstocks.

Tall Oil Biodiesel Feedstock

Crude tall oil (CTO) is a major by-product of the Kraft pulping process. CTO has proven to be an important source of raw chemical materials, as it consists mostly of resin and free fatty acids (see Figure 2).

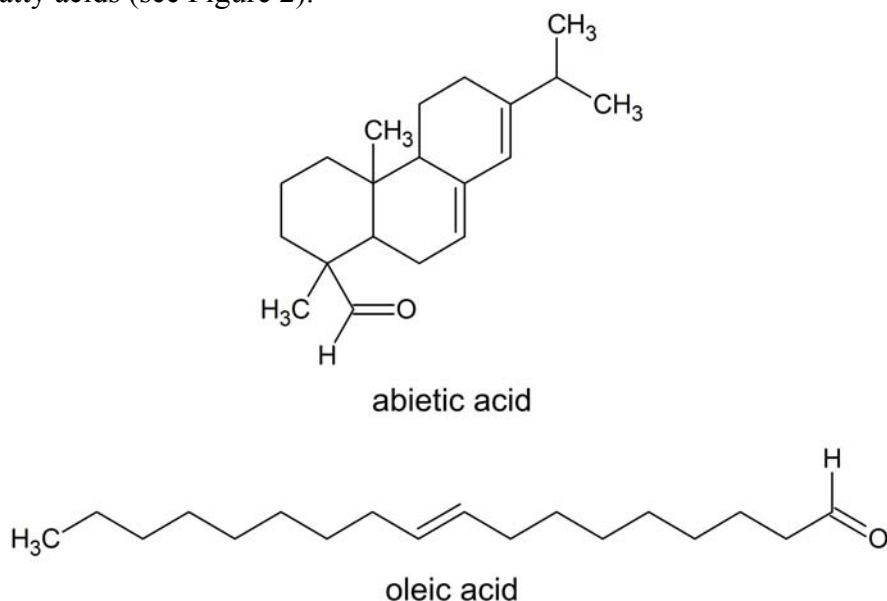


Figure 2. Examples of resin (abietic) and fatty (oleic) acids prominent in CTO

During pulping, wood chips (commonly pine) are cooked in an alkaline solution (white liquor) that saponifies the naturally occurring fatty and resin acids in the wood. After the cooking process, the spent solution (black liquor) contains the sodium salts, or soaps of the resin and fatty acids as well as some other neutral compounds. As the liquor is evaporated to efficiently reuse the pulping chemicals, the concentrated soaps float to the top and are easily skimmed off for collection. These skimmings are then converted to crude tall oil by acidification with sulfuric acid¹⁷.

The principal components of CTO include saturated and unsaturated C₁₈ free fatty acids, free resin acids, and other non-acidic compounds (sterols, bulky alcohols) commonly referred to as neutrals or unsaponifiables. The exact composition of CTO, however, can vary widely. In a study of pulping facilities in the southern U.S., it was found that while the time of year that the wood was harvested has little effect on the CTO composition, the geographic location, wood type, and age have a tremendous effect¹⁸.

Crude tall oil, for example, has been shown to have higher portions of fatty acids and unsaponifiabiles in some cases simply due to the use of other species such as birch or spruce^{19,20}. Depending on these factors, CTO could contain 30-50% free fatty acids, 40-50% resin acids, and 10-30% unsaponifiabiles. Some of the more common compounds in CTO include oleic acid, linoleic acid, abietic acid, β -sitosterol, and other diterpene alcohols. Figure 3 depicts composition profiles of crude tall oil for the southern U.S. and other geographic locations and illustrates how the composition may vary.

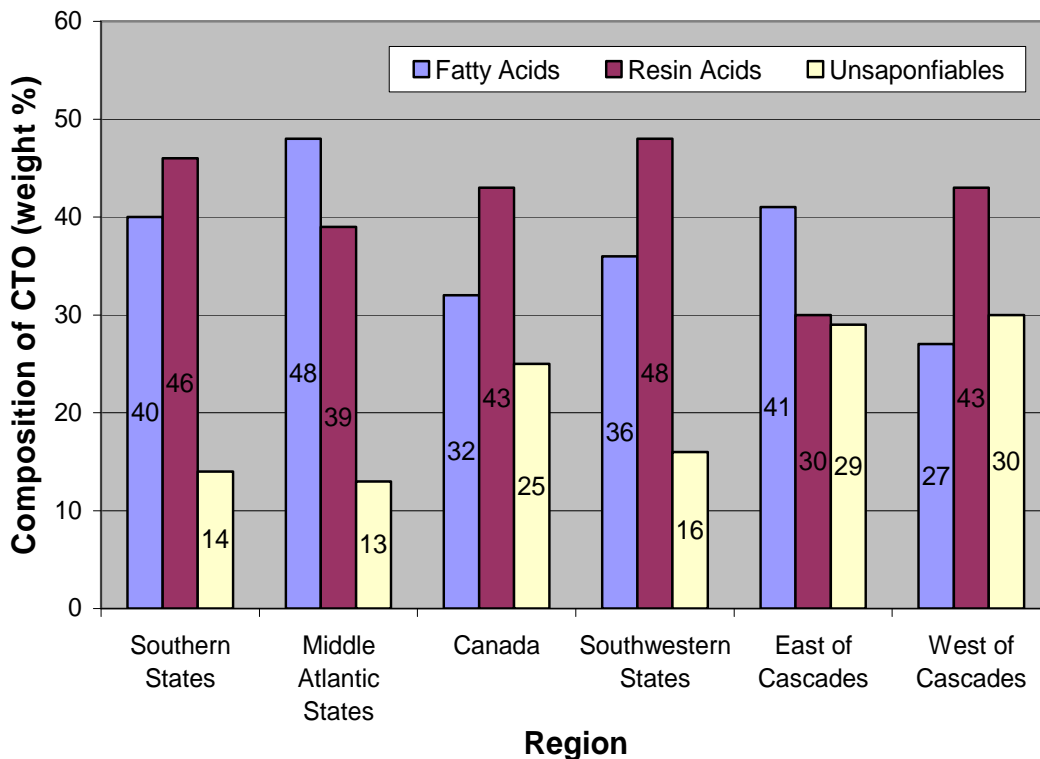


Figure 3. Geographical variation of crude tall oil composition

The resin acids in CTO are generally bulky molecules, much different from the straight-chained free fatty acids. As expected from the multi-ring structure, the methyl ester of the main resin acid, (abietic), has a high melting point (25°C) and boiling point (365°C). These are undesirable properties for use in biodiesel, especially when considering cold-flow behavior or residue build-up from the presence of high boiling compounds. On the other hand, properties of the methyl ester derived from one of the main fatty acids (oleic) are very similar to that of No. 2 diesel fuel²¹.

Based on data compiled from the U.S. Census Bureau²², the annual production of crude tall oil is approximately 1.2 billion pounds per year, of which about 90% goes through a distillation refining process²³. The CTO is upgraded by distillation to produce five major fractions: 1) heads, 2) tall oil fatty acids (TOFA), 3) distilled tall oil (DTO), 4) tall oil rosin (TOR), and 5) pitch. The heads product consists of the lower boiling

fractions such as palmitic acid and some neutral compounds, while the pitch fraction consists of mostly the higher boiling or nonvolatile unsaponifiable products. The DTO contains a mixture of fatty acids and resin acids that can vary in concentration. The two main products, TOFA and TOR, consist almost entirely of the respective fatty and resin acids.

After years of a U.S. CTO surplus, tall oil stockpiles have steadily decreased since 2003 as tall oil exports have increased. One major recipient of U.S. tall oil, Sweden, has taken advantage of the renewable resource, as refined tall oil is burned directly for energy²⁴. This is illustrative of the fuel potential the raw material holds. CTO contains approximately 50 % free fatty acid. The use of the refined components of CTO, especially the free fatty acid portion, broadens the biodiesel feedstock base thereby easing intermittent supplies.

Chicken Fat Feedstock

Based on data compiled from the U.S. Census Bureau, the annual production of poultry fat is approximately 1.3 billion pounds per year. A byproduct of poultry processing, chicken fat consists of mostly fatty triglycerides and can contain free fatty acids. Higher quality chicken fat is lighter in color and contains trace amounts of free fatty acids. The lower quality chicken fat, however, can be brown or even black in color and contain higher amounts of free fatty acid (> 3% by weight). Previous studies of triglyceride feedstocks with varying amounts of free fatty acids are well documented and will be discussed later. In particular, Mattingly²⁵ found chicken fat to be a low cost and high yield feedstock for biodiesel in his optimization study. Some problems encountered include product separation difficulties and catalyst consumption due to the saponification of free fatty acids present in the chicken fat.

The comparison of some various feedstock prices (October 2007) shown in Figure 4 illustrates the relative cost of TOFA, DTO, CTO, and chicken fat^{23,26,27,28,29}. TOFA, at 40 cents per pound, is competitive with refined soybean and rapeseed oils that are currently used to produce a majority of the biodiesel in the United States and Europe respectively. The higher quality chicken fat, at 25.4 cents per pound, is a much less expensive feedstock, as well as the lower quality type that costs 19.5 cents per pound. If fuel properties of resin ester-containing DTO- or CTO-derived biodiesel can be improved through blending, they are cost-competitive feedstocks, at 42.5 and 20 cents per pound respectively. Efficient conversion of blends of these feedstocks would lead to a simpler infrastructure of biodiesel production, as a biodiesel plant with this process technology capability could handle a variable quality feedstock.

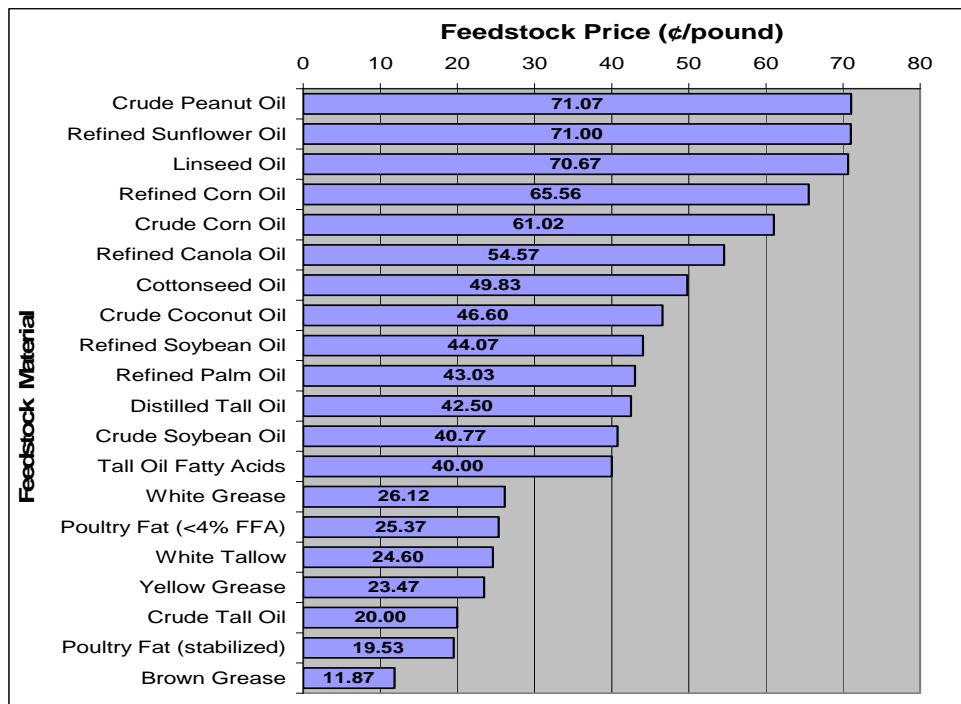


Figure 4. Prices of potential biodiesel feedstocks, (October 2007)

Traditional Biodiesel Production Techniques

Numerous production techniques and procedures have been proposed to convert feedstock triglycerides and free fatty acids into the alkyl esters that make up biodiesel. Some common techniques used include the base-catalyzed transesterification of triglycerides, the acid-catalyzed esterification of free fatty acids, and an acid/base combination of catalysts for sequential esterification/transesterification reactions. Most of the methods and procedures for biodiesel production depend greatly on the quality and content of the feedstock, especially with respect to free fatty acid content.

Since most of the biodiesel produced today originates from refined vegetable oils that contain mostly triglycerides and little free fatty acids, the base-catalyzed transesterification method depicted in Figure 5 is the most commonly used production process. Though acid-catalyzed transesterification of the triglycerides is feasible, the harsh reaction conditions and long reaction times required favor the base-catalyzed reaction³⁰. It has been shown that the alkaline catalyst (commonly NaOH or KOH) is effective in transesterifying the triglycerides present, but is ineffective in esterifying free fatty acids. In this transesterification reaction, an ester and an alcohol (i.e. methanol) react to form a different ester. The three fatty acid chains (R_iCOO^-) connected to the glycerol backbone are broken at their ester bond and react with the alcohol to form alkyl esters and a glycerol molecule:

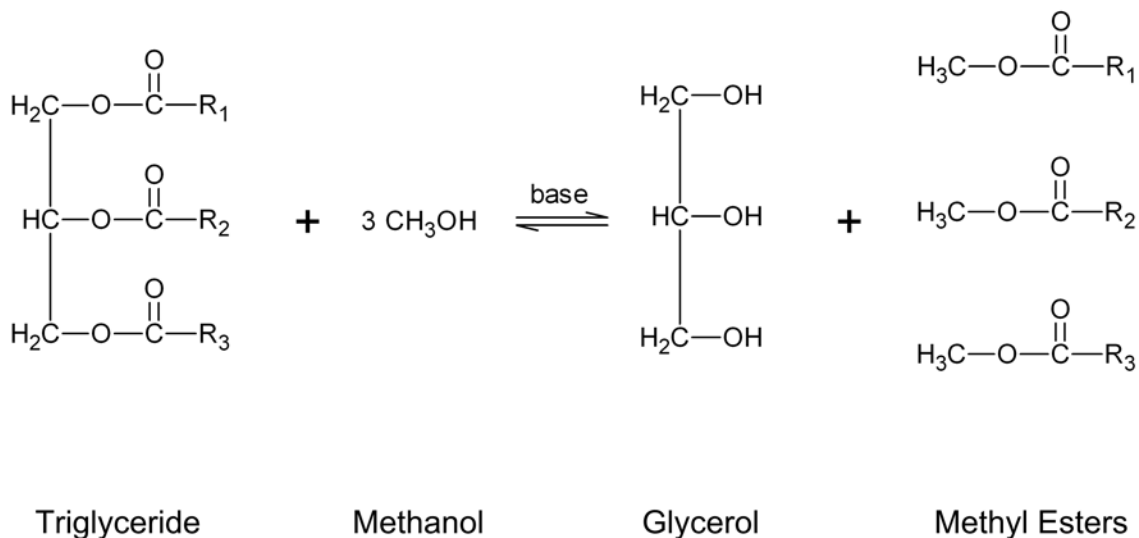


Figure 5. Base-catalyzed transesterification reaction

This transesterification reaction with vegetable oils for biodiesel production has been the subject of many reviews and research papers. Such papers investigate the effect of various reaction parameters on the reaction kinetics, including the molar ratio of alcohol to feed oil, catalyst type and concentration, reaction temperature, reaction time, moisture content, and the presence of free fatty acids. While clearly effective for refined feedstocks, Canakci and Van Gerpen found that the presence of free fatty acids in the feedstock at concentrations greater than 1-2%, as typically found in less refined materials, causes a variety of problems with this reaction and greatly decreases the biodiesel yield⁵. These problems, also noted in other studies, include catalyst depletion, soap formation, and separation difficulties due to the saponification reaction shown in Figure 6 :

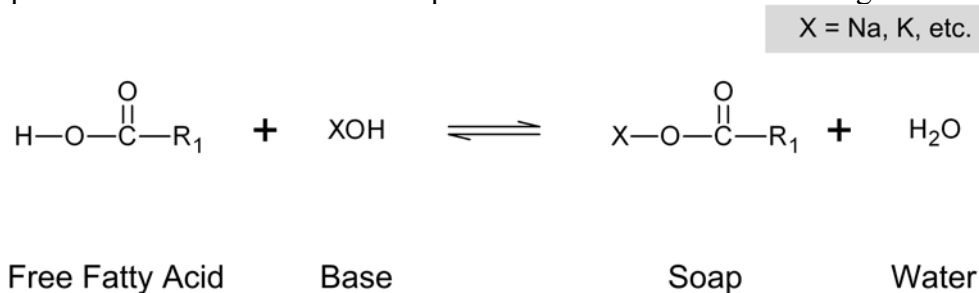


Figure 6. Undesired saponification reaction

With regards to the chicken fat feedstocks under investigation herein, Mattingly found that lower quality chicken fats that had a high free fatty acid content exhibited many of these problems. Furthermore, since tall oil components are rich in free fatty acids, with few triglycerides present, the transesterification pathway, though proven and reliable, is inappropriate for the production of biodiesel from tall oil feedstocks.

Since many feedstocks contain amounts of free fatty acids greater than 2%, an effective and efficient means for converting these into alkyl esters is required. As mentioned earlier, acid catalysts (Figure 7) are ineffective in the transesterification of triglycerides, but they have proven to be effective in the esterification of free fatty acids:

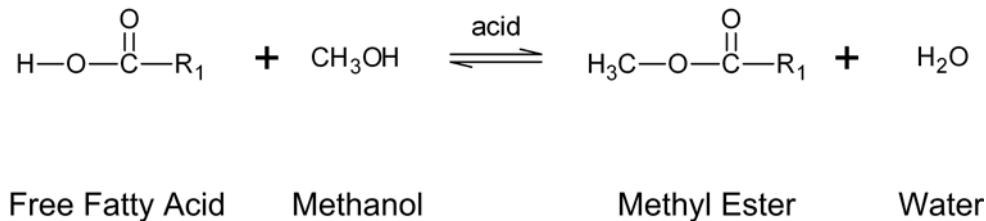


Figure 7. Acid-catalyzed esterification reaction

It is important not to confuse the ineffective acid-catalyzed transesterification with the effective acid-catalyzed esterification. Transesterification refers to the reaction of an ester with an alcohol to form a different ester, while esterification refers to the reaction of an acid with an alcohol to form an ester.

In the esterification reaction, a free fatty acid reacts with a large excess of alcohol (i.e. methanol) to form an alkyl ester and water in the presence of an acidic catalyst (usually H₂SO₄). Jaayaraj et al.³¹ effectively esterified the free fatty acids found in rubber seed oil using sulfuric acid as a catalyst. The acid content decreased from 17% to less than 2% during the esterification. The remaining triglycerides in the oil were then transesterified using an alkaline catalyst as described above. Many others have treated high-free fatty acid-containing triglyceride feedstocks with this multi-step conversion technique with similar results²⁵. Di Serio et. al.³² further proposed a reliable kinetic rate expression for the esterification of a free fatty acid (oleic acid) in the presence of triglycerides. From batch reactor experiments (no product removal), they determined that the reaction proceeded rather quickly and conversions in excess of 80% were possible.

Taking a different approach, Haas³³ hydrolyzed all triglycerides present in a lower quality soybean oil to form free fatty acids and glycerol, as depicted in Figure 8. After removing the glycerol, he then esterified the resultant mixture of fatty acids via acid catalysis. In his economic analysis, he concluded that producing biodiesel from these lower value feedstocks was 25% less expensive to produce than from refined soybean oil even after including the additional costs for processing the lower quality materials.

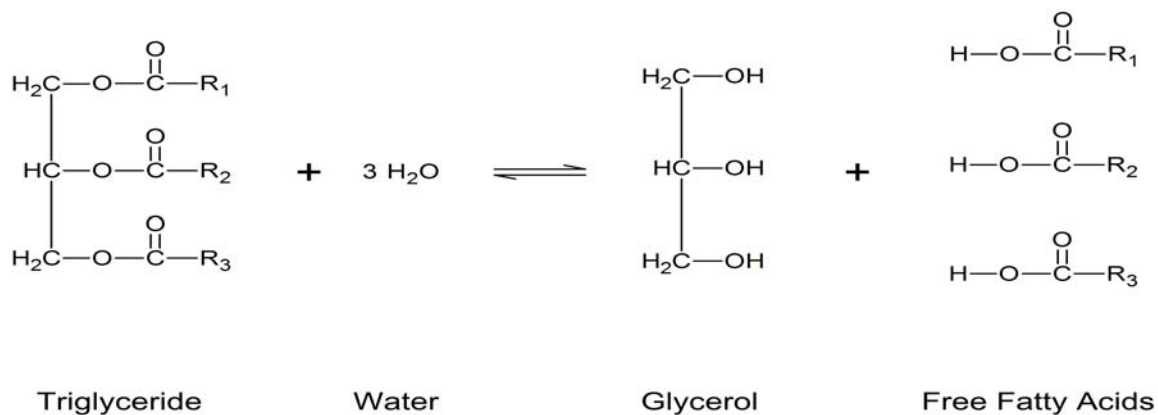


Figure 8. Hydrolysis of triglycerides

The esterification reaction is reversible thus as the reaction proceeds, water is produced thereby inhibiting the forward reaction. This is illustrated by the 80% conversions to which Di Serio et al. were limited. At equilibrium, enough water is formed to prematurely stop the production of methyl esters, leaving a large quantity of unreacted materials. Canakci and Van Gerpen determined that as little as 0.1% (by weight) of water in the reactants could reduce methyl ester production. They found that the addition of only 5% water reduced the total reactant conversion to less than 6% (as opposed to 95% conversion without water.) This gives a very low tolerance to water for the acid-catalyzed reaction. In further work, they found that by performing the esterification reaction in multiple stages, with a water removal step in between, the reaction time as well as the catalyst and alcohol use could be significantly reduced. Otherwise, the alcohol to feed ratio is commonly in excess of 30:1. This illustrates how this multiple-step approach can significantly reduce material costs. Steinigeweg and Gmehling³⁴ used a novel process known as reactive distillation to effectively esterify a free fatty acid feedstock, reduce the required alcohol and catalyst amounts, and purify the products in the same unit operation. This method allows for continuous removal of water and esters, which drives the reaction to completion, but still relies on the use of the acidic catalyst.

In comparison to base-catalyzed transesterification, this acid-catalyzed method is much more applicable to tall oil conversion considering that TOFA and CTO have high concentrations of free fatty acids. However, the acid-catalyzed transesterification of triglycerides in the chicken fat would demand very long reaction times as mentioned earlier. In general, for the esterification reaction, the major obstacles to overcome are catalyst separation and recovery, the removal of water to drive the reaction to completion, and the long reaction times required with the presence of triglycerides.

Supercritical Methanol Treatment

At ambient conditions, triglycerides and free fatty acids, which are both relatively non-polar compounds, are not very soluble in methanol, a well-known polar compound^{35, 36}. Therefore, when methanol is combined with triglycerides or free fatty

acids without the use of an alkali or acidic catalyst (respectively) the reaction system is essentially heterogeneous. Thus, two insoluble phases are formed, allowing very little contact between the reactants. This lack of intimate contact explains the long reaction times, in excess of 10 hours, that are required for biodiesel production without the use of a catalyst³⁷. The addition of catalyst helps promote the nucleophilic attack of methanol on the carboxyl group(s) in the feedstock, increasing the reaction rates for esterification or transesterification³⁸. Other heterogeneous chemical catalysts have a similar functionality, while enzymatic catalysts rely on highly selective active sites on their surface that perform the reaction(s).

These various catalytic processes of transesterification, esterification, and hydrogenation can involve feedstock pretreatment, multiple reaction steps, recovery of unreacted reactants, purification of the alkyl esters, catalyst consumption or inactivation, and difficult separation (and possible regeneration) of catalyst from the reaction mixture. These steps can make the overall process expensive and complicated. It can also lead to extraneous waste streams. For these reasons, non-catalytic conversion of vegetable oils was investigated. There exists a novel process for biodiesel production that offers intimate contact between the renewable feedstock and methanol without the use of any catalyst. Recent proponents of the process have termed it supercritical methanol treatment.

In supercritical methanol treatment, feedstock and methanol are charged to a reactor in which they are subjected to temperatures and pressures beyond the critical point of methanol ($T_c = 240\text{ }^\circ\text{C}$, $P_c = 1,140\text{ psia}$, see Figure 9). The basic concept of supercritical methanol treatment is based on the effect of temperature and pressure on the thermophysical properties of methanol, such as viscosity, diffusivity, density, and polarity^{39, 40}. When treated beyond its critical point, methanol no longer has a distinct liquid or vapor phase, but rather a single fluid phase. With this phase change, methanol possesses an increased mass diffusivity, decreased viscosity, and a density that can be manipulated over a large range through relatively small changes in temperature and pressure. These fluid properties allow supercritical methanol to be used as a tunable solvent with superior mass transfer characteristics.

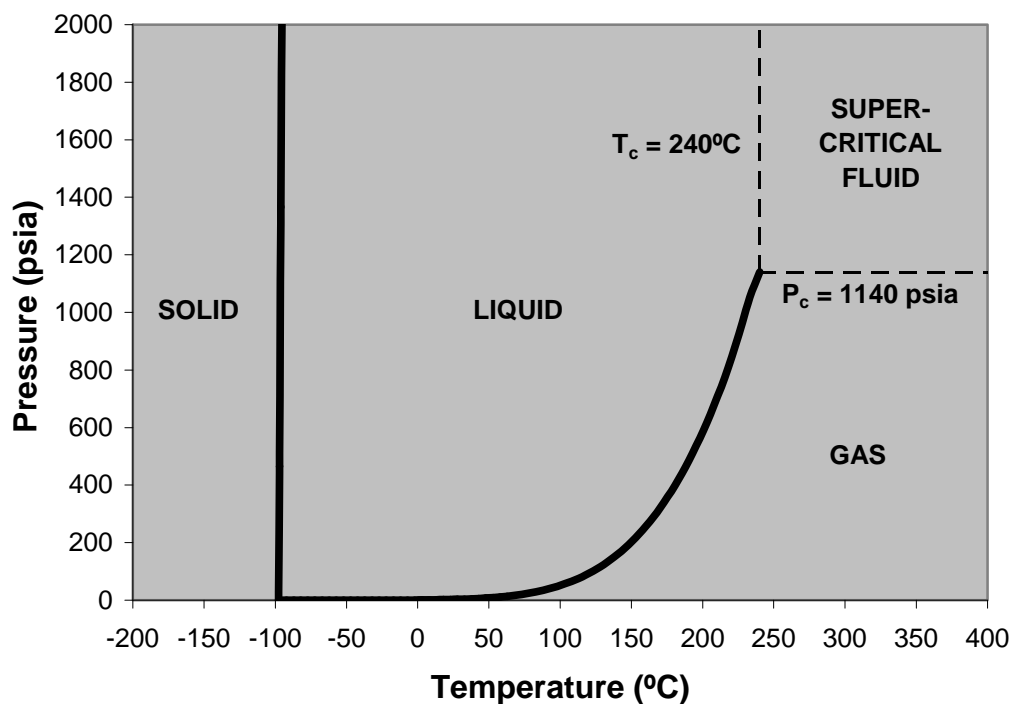


Figure 9. Phase diagram for methanol⁴¹

A measure of a solvent's polarity, the dielectric constant of methanol also decreases in the supercritical state⁴², which suggests that supercritical methanol behaves more like a non-polar compound. This, in turn, suggests that the non-polar feedstocks for biodiesel might be better solvated in methanol in its supercritical state, greatly increasing the contact between the two.

The solvent strength of methanol and any other solvent can be quantified by its solubility parameter. There are multiple correlations for predicting the solubility parameter of a substance, such as the simple Hildebrand parameter, or the generally more accurate but more complex Hansen parameter. More detail on this solubility parameter theory can be found in the publications of Hildebrand⁴³ or Hansen⁴⁴. The solubility parameter relies heavily on the temperature and pressure of the substance, as outlined by Williams⁴⁵. Table 1 gives values for the Hansen parameters at ambient conditions (experimental) as well as for a supercritical state of methanol (calculated).

Table 1. Comparison of solubility parameters

| Substance | Temperature (C) | Pressure (psia) | Solubility Parameter ⁴⁶ (J/cm^3) ^{1/2} |
|---------------|-----------------|-----------------|--|
| Methanol | 25 | 14.7 | 29.61 |
| Soybean Oil | 25 | 14.7 | 17.37 ⁴⁷ |
| Oleic Acid | 25 | 14.7 | 15.60 |
| Water | 25 | 14.7 | 47.90 |
| Methanol | 300 | 1650 | 7.93 |
| Soybean Oil | 300 | 1650 | 5.96 |
| Oleic Acid | 300 | 1650 | 10.66 |
| Water | 300 | 1650 | 27.56 |
| Methyl Oleate | 25 | 14.7 | 15.46 |
| Glycerol | 25 | 14.7 | 36.16 |

While maximum solubility occurs when the solubility parameter of the solute (i.e. vegetable oil or animal fat) matches that of the solvent (i.e. methanol), miscibility occurs when they are within ~ 5.2 (J/cm^3)^{1/2} ⁴⁸. At ambient conditions, the solubility parameter of methanol (29.6) differs significantly from that of soybean oil (17.4) and oleic acid (15.6). This may explain their immiscibility without the use of a catalyst. On the other hand, the solubility parameter of methanol under supercritical conditions (7.93) matches favorably with that of soybean oil (triglyceride-based) and oleic acid (a free fatty acid) at 5.96 and 10.66, respectively at these conditions. This further suggests a greater solubility of these feedstocks in supercritical methanol. The solubility ranges of methanol for the two conditions are better illustrated in Figure 10. This increased solubility at higher temperatures and pressures allows methanol to act as a solvent as well as a reactant in the transesterification of triglycerides and the esterification of free fatty acids.

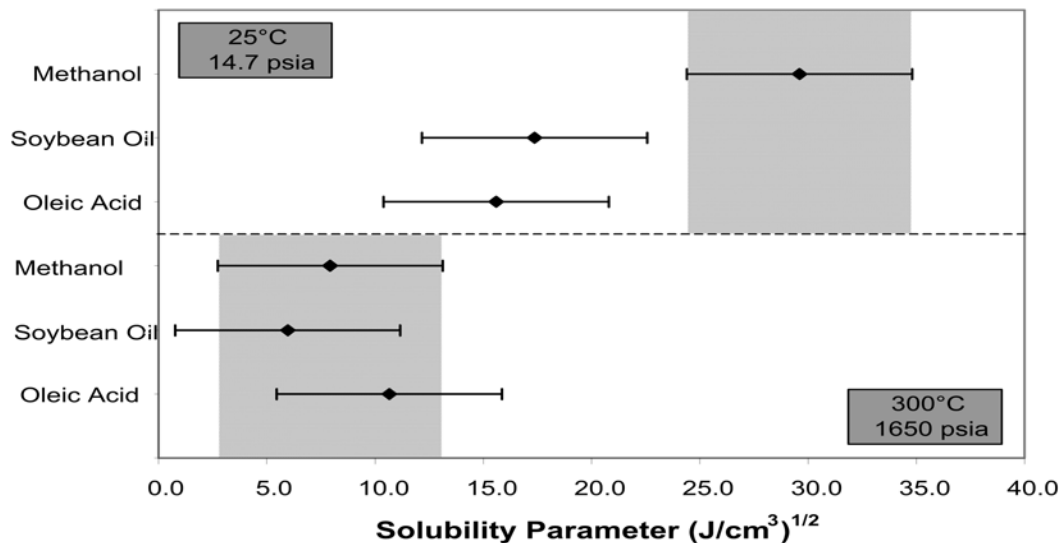


Figure 10. Hansen solubility parameters for two physical states with miscibility ranges indicated

Supercritical methanol treatment has reportedly been used to produce methyl esters (biodiesel) from various feedstocks. Therefore, unlike the chemical-catalyzed methods, this process requires no separate catalyst for biodiesel production. This key advantage offers a simpler process without catalyst regeneration or recovery, catalyst consumption by free fatty acids, or reaction inhibition by water, which the conventional processes suffer from.

The use of supercritical methanol treatment for biodiesel production was conducted in Japan and published as early as 2001. Kusdiana and Saka used a batch reactor vessel to transesterify rapeseed oil triglycerides with methanol at various temperatures and pressures ranging from 350-400°C and 6,530-9,430 psia, very extreme conditions. These experiments were conducted with a constant and excess molar ratio of methanol to oil of 42:1, while the stoichiometric ratio is 3:1. At 350 °C ($T_r = T(K)/T_c(K) = 1.21$) and 8,700 psia ($P_r = P/P_c = 7.63$), it only took 240 seconds of supercritical treatment to result in a 95% conversion of rapeseed oil to methyl esters. Not only was supercritical treatment faster than the conventional catalyzed methods, but product separation was much easier in that there was no soap formation or catalyst recovery involved.

In a subsequent study of the reaction kinetics of the transesterification of rapeseed oil, it was determined that the molar ratio of methanol to rapeseed oil was one of the most important variables affecting the yield of methyl esters. At a molar ratio of 42:1, nearly complete conversion was found after 240 seconds of treatment, whereas with a molar ratio of 3.5:1 and at the same treatment time, the yield of methyl esters dropped to 55%. The results indicated that higher molar ratios of methanol result in a more complete transesterification reaction, perhaps due to the increased contact area between methanol and the triglycerides.

In the same kinetics study, Kusdiana and Saka also investigated the effect of temperature on the rate constant for formation of methyl esters. At temperatures of

200°C ($T_r = 0.922$) and 230°C ($T_r = 0.981$), low conversions and long reaction times were observed, most likely attributable to the subcritical state of methanol ($T_r < 1$). These results compare favorably with Diasakou's study of non-catalyzed transesterification in methanol at conditions below the critical point. Even at a temperature of 270°C and 1750 psia, ($T_r = 1.06$, $P_r = 1.54$), and a treatment time of 1,000 seconds, only a 50% yield of methyl esters was obtained. This could be due to the instability of the supercritical state at this temperature. At 300°C and 2,030 psia, ($T_r = 1.12$, $P_r = 1.78$), a considerable change in the conversion rate was seen, as it took only 240 seconds to obtain an 80% yield of methyl esters. At a higher temperature of 400°C, thermal degradation was found to take place, defining an optimal temperature range for supercritical treatment of 300-350°C⁴⁰.

Kusdiana, et al. later questioned the effect of pressure on the rate of reaction⁴⁹. They noted that the ionic product of methanol, a thermophysical property that greatly affects its reactivity, increases with increasing pressure. This led the group to suggest that the methanol itself acts as an acid catalyst in the supercritical transesterification reaction. Choi, et al. verified that increasing the reaction pressure increases the reaction rate to an extent⁵⁰. At a specified treatment time and set of reaction conditions, while there was essentially no methyl ester formation below 730 psia ($P_r = 0.64$), the yield of esters increased linearly to 90% at 4,350 psia ($P_r = 3.82$). Beyond this pressure, no benefits were realized. Other studies found similar results^{51, 52, 53, 54}.

He, et al. attributed these findings to the transition-state theory, which assumes the transitory formation of an activated complex from the reactants, and describes the effect of pressure on the apparent activation energy of the reaction. It was found that the significant difference between the partial molar volumes of the transition state complex and the reactants greatly affects the apparent activation energy, and thus the reaction kinetics, up to a pressure of roughly 4,500 psia^{53,55}. This maximum pressure is very similar to that suggested by Choi, et al. Glisic, et al. noted the increase in kinetic rates with increasing pressure as well and provided a possible explanation for this large difference in molar volumes⁵⁶. At ambient conditions the high degree of hydrogen bonding results in large aggregates of methanol, resulting in high densities. As shown in Figure 11, however, at supercritical conditions the molar density of methanol is greatly reduced from that at ambient conditions, which corresponds to a decrease in hydrogen bonding to form smaller or even monomeric methanol. It was suggested that a reaction mechanism involving a transition state of these smaller species could explain the increase in reaction rates, as they would provide better contact with the other reactants. Note that this is in strong agreement with the findings of He, et al. Based on these results, the direct relationship between pressure and the esterification/transesterification reaction rate has been found to be significant and cannot be ignored with large pressure differences.

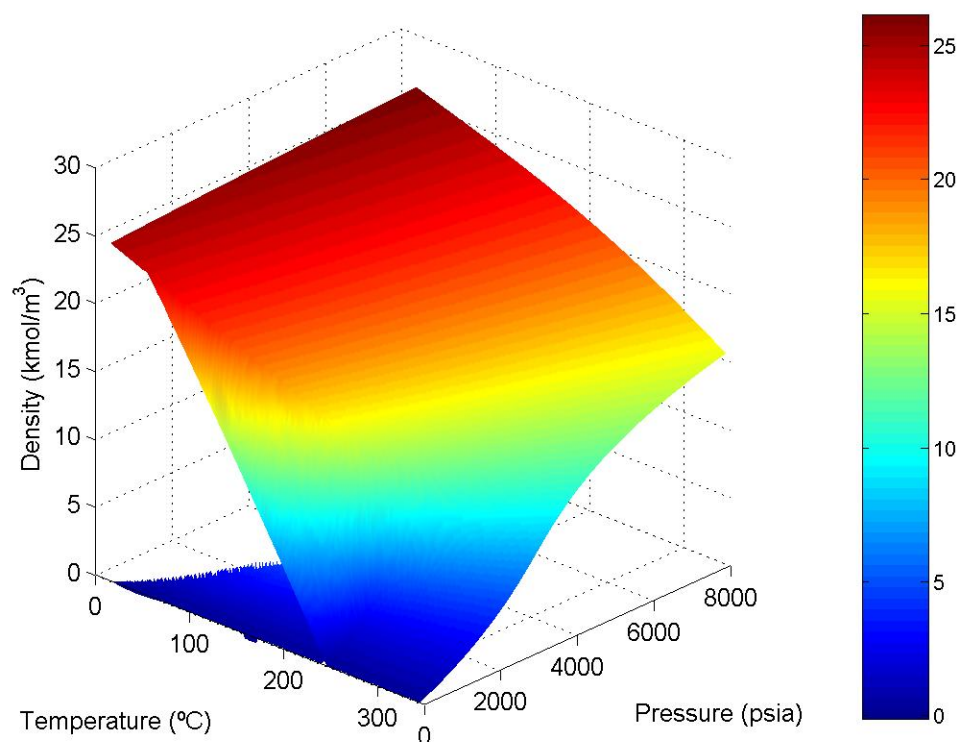


Figure 11. Methanol density as a function of temperature and pressure

In further work, Kusdiana and Saka demonstrated that free fatty acids could be esterified during supercritical methanol treatment⁵⁷. In fact, it has been shown that esterification of free fatty acids occurs at an even higher reaction rate than the transesterification of triglycerides⁵⁸. In another kinetic study involving free fatty acids, Madras and Varma further showed that reaction rates are slightly higher for those that are saturated and slower for those with one or more double bonds⁵⁹. This relationship was also shown to be true for triglycerides. Therefore, whereas the more common acid and base-catalyzed reactions work well for conversion of free fatty acids or triglyceride oils (respectively), supercritical treatment is able to convert both into methyl esters in a single step process without pretreatment, an important advantage over the other production methods^{39, 51, 60}.

While it has been shown that other biodiesel production methods are adversely affected by the presence of water in the reaction system, water has been found to have no negative effects on the supercritical conversion of triglycerides or free fatty acids to methyl esters⁶¹. In fact, it has been shown that at higher temperatures and pressures, water will solublize non-polar compounds more readily, further encouraging a single-phase reaction system. Additionally, triglycerides can be hydrolyzed to free fatty acids and glycerol under these conditions, which is advantageous as esterification of the former

is relatively faster than the transesterification of triglycerides. The presence of water was also found to be advantageous as it made the separation of methyl esters from the glycerol by-product easier, since glycerol is more soluble in water (see Table 1). In contrast, testing the effect of water content on conventional acid/base catalyzed reactions showed that water in the reaction mixture greatly decreased methyl ester yields. This illustrates other important advantages that supercritical treatment holds over other methods of biodiesel production in that no water-caused emulsions are formed and the reaction is not inhibited by water as in the base and acid/enzyme catalyzed methods, respectively. These findings further suggest that mixtures of feedstocks, including low-value or waste oils that have higher water contents that are not applicable to the catalyzed methods, could be used for biodiesel production in non-catalytic supercritical methanol treatment, while still achieving high conversions.

Since the previous studies had shown that high temperatures (350°C), pressures (>4,000 psia), and molar ratios of methanol (42:1) could be required for supercritical methanol treatment, Cao, et al. investigated the use of propane⁶² and carbon dioxide⁶³ as co-solvents in an effort to reduce these reaction conditions. It is believed that the addition of an appropriate co-solvent can increase the mutual solubility of methanol and vegetable oil at lower reaction temperatures. At a methanol to oil ratio of 33, a reaction time of 10 minutes, a pressure of 2,300 psia ($P_r = 2.02$), and a temperature of 270°C ($T_r = 1.06$), it was found that without the use of a co-solvent, only a 22% yield of methyl esters was obtained. However, with a molar ratio of co-solvent to methanol of 0.1, the methyl ester yield increased to 90% and 85% for propane and carbon dioxide, respectively. The optimal reaction conditions determined by these two studies call for a methanol to oil ratio of 24, a CO₂ to methanol ratio of 0.1, and a 10 minute reaction time at 280°C ($T_r = 1.08$) and 2,000 psia ($P_r = 1.75$) which gave a methyl ester yield of over 98%. These results demonstrate how the use of a co-solvent can greatly reduce the harsh reaction conditions required in supercritical methanol treatment.

Various research groups have investigated the substitution of longer alkyl chain alcohols (C₂-C₈) for use in the supercritical process. It has been demonstrated that while the more expensive, longer chained alcohols require longer treatment times⁶⁴, the optimal reaction pressure is reduced, due to the lower critical pressures of the alcohols. This presents a unique cost optimization between the choice of feedstock and the size and rating of the reaction vessels. The use of bio-ethanol, in particular, as the reacting alcohol presents an interesting possibility as the produced biodiesel could be completely derived from renewable resources. Important to note also is that biodiesel produced from the longer chained alcohols has also been shown to give superior cold flow properties, such as reduced cloud and pour points, as well as several other fuel characteristics.

Most of the more recent work with supercritical methanol treatment has been aimed at improvements for production scale implementation. Anitescu, et al. designed several different sized biodiesel plants. Based on a feedstock of refined soybean oil and without the use of any unique heat recovery schemes, they found that the cost of biodiesel fuel from supercritical methanol treatment could range from \$2.49 to \$3.46 per gallon, depending on the plant capacity⁶⁵. These prices indicate that supercritical methanol treatment of refined soybean oil could be price-competitive with the traditional base-catalyzed method (then \$2.60/gallon) suggesting that the costs of elevated temperature

and pressure are more than offset by benefits of a catalyst free system with simple product separation. An initial estimate shows that the energy consumed during this heating and pressurization of the feedstocks is approximately 8.1% of the final fuel's energy content. The cost of biodiesel using less refined materials has not yet been compared for the two processes.

Several research groups have studied continuous flow tubular reactor systems using supercritical methanol treatment. A majority of the results confirm optimal temperatures, pressures, and methanol ratios found in previous batch-reactor studies^{50,51}. Busto, et al. experimentally determined optimal flow characteristics represented by the Peclet number (a ratio of convection and diffusion effects) in an attempt to reduce the detrimental effects of back-mixing⁶⁶. Their results are important for the proper and efficient design of tubular reaction vessels. He, et al. identify a critical reactor residence time of the reactants based on the reaction temperature. Above this critical residence time, even at just 300°C, thermal degradation of the methyl esters was found to occur. To solve this problem, they developed a gradual heating reaction process, where a temperature gradient over the tubular reactor is used. This eliminated thermal degradation and resulted in high methyl ester yields (>95%).

Taking advantage of a faster reaction with free fatty acids, Kusdiana and Saka proposed a two-step process utilizing supercritical methanol⁶⁷. In the first step, all triglycerides present in the feedstock were hydrolyzed to free fatty acids and glycerol using subcritical water. After phase separation to remove glycerol, these fatty acids were then treated with supercritical methanol in the second step to form biodiesel. Though the additional hydrolysis step is required, this process has reportedly given greater yields of methyl esters, shorter reaction times, and has reduced the temperature, pressure and excess methanol requirements, requiring less energy for the process⁶⁸. D'Ippolito et al. modeled this two-step procedure and incorporated heat recovery systems⁶⁹. Their model suggested that the heat duty could be reduced by 37% from the single-stage supercritical process due to the less severe reaction conditions and heat recovery schemes.

This two-step procedure, sometimes referred to as the Saka-Dadan process, is currently being developed for commercial applications under the "High Efficiency Bioenergy Conversion Project" sponsored by New Energy and Industrial Technology Development Organization (NEDO)⁷⁰. Initial reports suggest the hydrolysis and esterification reactors will both be operated at 270 °C and 1,020 psia, both reasonable for industrial application⁷¹. As of 2003, a bench-scale plant had been successfully operated. In the establishment of the commercial process, the project scope includes fundamental studies on the reactions, resultant fuel properties, automatic control systems, any pre- or post-treatment requirements, as well as a business model on biodiesel and a market study on the oil/fat feedstocks as well as biodiesel fuel.

Table 2 lists some advantages and disadvantages of each of the discussed biofuel production methods. While supercritical methanol treatment does have some disadvantages, all those listed in the table can be alleviated through the use of a co-solvent such as carbon dioxide, or the additional hydrolysis step. The criteria included in the selection of this method for the conversion of tall oil and chicken fat into biodiesel included the capability to convert triglycerides and free fatty acids, required reaction time, reaction inhibition, catalyst inhibition, catalyst requirements, and pretreatment

requirements. Based on these criteria, supercritical methanol treatment was a promising technique for this investigation.

Table 2. Comparison of various biodiesel/diesel substitute production methods

| Biodiesel Production Method | Advantages | Disadvantages |
|------------------------------------|---|---|
| Base-Catalyzed Transesterification | <ul style="list-style-type: none"> • Proven • Low temperature, ambient pressure • Short reaction times with triglycerides • Low methanol:oil ratio (~6) | <ul style="list-style-type: none"> • Inhibited by FFA contents >0.5% • Requires refined feedstocks • Product separation difficulties • Catalyst neutralization/recovery |
| Acid-Catalyzed Esterification | <ul style="list-style-type: none"> • Proven • Low temperature, ambient pressure • Short reaction times with FFA • Effective pretreatment for high FFA feedstocks | <ul style="list-style-type: none"> • Inhibited by water • High methanol:oil ratio (~40) • Slow reaction with triglycerides • Catalyst neutralization/recovery • Corrosion-resistant materials required |
| Enzyme Catalysis | <ul style="list-style-type: none"> • Low temperature, Low pressure • Treats FFA and triglycerides • Essentially pure product, no by-products • Simple product recovery • Low methanol:oil ratio (~4) | <ul style="list-style-type: none"> • Long reaction time • Expensive enzymes • Enzyme inactivation (water) |
| Hydroprocessing | <ul style="list-style-type: none"> • Proven • Treats FFA and triglycerides | <ul style="list-style-type: none"> • High temperature, moderate to high pressure • Pretreatment/Post-treatment (isomerization) • Eliminates beneficial properties • Catalyst coking, poisoning, regeneration • By-products |
| Supercritical Methanol Treatment | <ul style="list-style-type: none"> • Treats FFA and triglycerides • No catalyst required • Not inhibited by water • Simple product separation • Short reaction times | <ul style="list-style-type: none"> • High temperature, high pressure without cosolvent • High methanol:oil ratio (~40) without cosolvent |

Equipment Used For This Study

A Parr Instruments 4520 series, 2-L reactor (1), made of tempered 316-stainless steel and rated at 350°C and 1,900 psia, was employed in this study and is shown in Figure 12. A 1,500-watt, Calrod-type shelled element heater (2) was used to quickly reach supercritical temperatures. The reactor temperature was measured with a type-J, sheathed thermocouple (3) installed in a thermowell (4) that extended the length of the vessel and was monitored with an Omega HH82A thermocouple reader (5). The pressure was measured with a 0-2,000 psi pressure gauge (6) installed on the vessel head. Twin 2.25" diameter, 6-blade, 45°-pitched impellers (7) were attached to a magnetic drive shaft (8) which was turned by a 1/20 HP GK Heller heavy duty variable speed lab stirrer (not shown). This enhanced agitation inside the vessel. To prevent the magnetic drive from overheating, cooling water was circulated through an incorporated cooling sleeve (not shown). A spiral cooling-coil (9) was installed to quickly cool the reactor contents with a supply of cooling water (10), thus quenching the reaction at the end of each trial. A dip tube (11) extending the length of the reactor was connected to a valve (12) to allow for liquid sampling, but was not used in this study. Also on this fitting was a gas inlet angle valve (13) for inerting the reactor and clearing the dip-tube. Another angle valve (14) allowed for gas sampling or gas pressure relief. Finally, a burst disc (15) rated at 1,920 psia (325°C) was installed to prevent the system pressure from reaching unsafe levels for the reaction vessel.

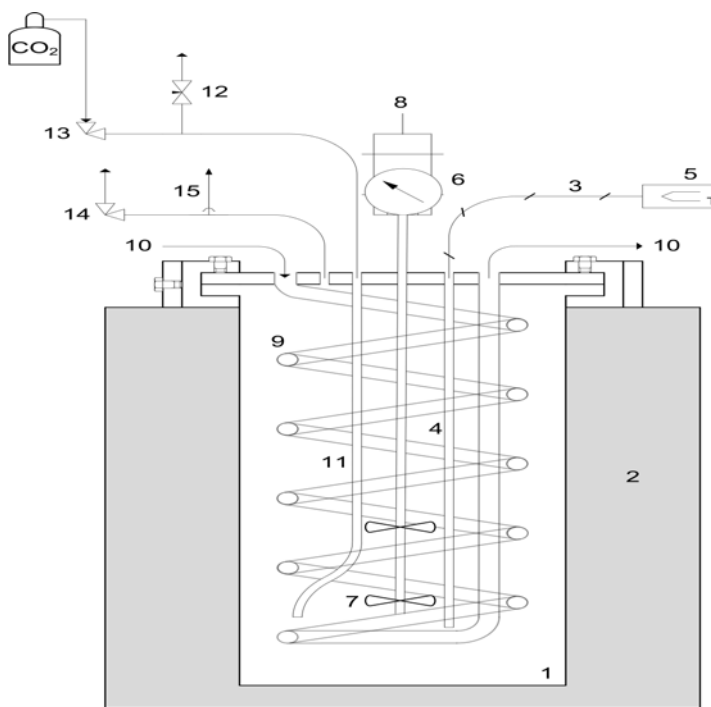


Figure 12. Supercritical reaction system and reactor schematic

Testing Conditions

There are many important variables that affect the performance of supercritical methanol treatment. Some include the reactor pressure, reaction temperature, methanol to feedstock ratio, and the reaction time.

The reaction temperature and methanol/feedstock ratio have been identified as two of the most important parameters with regards to costs in a large-scale biodiesel production with supercritical methanol treatment. Optimization of these parameters could 1) minimize the energy required to heat and pressurize the reactants, 2) lower methanol requirements, 3) lessen separation requirements, 4) minimize reactor volumes, and/or 5) increase production rates. A range was defined for the value of these two parameters based on previous work with supercritical treatment found in the literature. These test ranges are displayed in Table 3 and Table 4 presents certain physical properties of the pertinent compounds.

For the current study, the reaction time and pressure were held constant to determine effects of temperature and methanol use only. A pressure of 1,650 psia, well above the critical pressure of methanol ($P_r = 1.45$), was selected based on the maximum allowable working pressure of the reactor vessel. While lower than most used in previous literature, a pressure of 1,650 psia is more feasible in industry, and thus leads to more pertinent biodiesel yield characteristics if the supercritical process were used today. A mass of water equal to the feedstock was used to simulate lower quality feedstocks that typically may have higher moisture content, address issues of methanol flammability, reduce methanol requirements, and aid in product separation without impact on biodiesel yield potential. Also, a supercritical treatment time of 20 minutes was used for each of the experiments. The reaction temperature was tested in the range of 275-325°C, within the supercritical conditions for methanol, but below levels of thermal degradation. Finally, the molar ratio of methanol to feed oil/fat was tested between 10:1 and 40:1. The selection of these conditions was supported by the previous studies with this process. The proper reactor charge was estimated with an iterative procedure using the Peng-Robinson equation of state assuming single phase behavior.

Table 3. Testing conditions for supercritical methanol treatment

| Experimental Parameter | Testing Conditions |
|---------------------------------------|---------------------------|
| Reaction Time | 20 minutes |
| Reaction Pressure | 1,650 psia |
| Reaction Temperature | 275-325°C |
| Methanol to Feedstock Ratio (mol/mol) | 10-40 |

Table 4. Critical properties of pertinent compounds⁷²

| Component | Molecular Weight | Critical Temperature (°C) | Critical Pressure (psia) | Acentric Factor |
|------------------|------------------|---------------------------|--------------------------|-----------------|
| Myristic Acid | 228.4 | 492 | 246.7 | 0.935637 |
| Myristoleic Acid | 226.4 | 491 | 245 | 0.93 |
| Palmitic Acid | 256.4 | 512 | 219.1 | 0.982707 |
| Palmitoleic Acid | 254.4 | 512 | 219 | 0.98 |
| Stearic Acid | 284.5 | 531 | 197.4 | 1.03597 |
| Oleic Acid | 282.5 | 508 | 201.7 | 1.18222 |
| Linoleic Acid | 280.4 | 502 | 204.6 | 1.176 |
| Linolenic Acid | 278.4 | 507 | 209 | 1.18697 |
| Triolein | 884 | 705 | 48.5 | 1.987 |
| Methanol | 32.04 | 239 | 1173.1 | 0.565831 |
| Water | 18 | 374 | 3200 | 0.344861 |
| Carbon Dioxide | 44 | 31 | 1071.4 | 0.223621 |

Supercritical Methanol Treatment of Chicken Fat

The purpose of this portion of the study was to test chicken fat to determine the effect of reaction parameters such as temperature and the methanol to oil ratio, and which conditions give the greatest yield of biodiesel for supercritical methanol treatment. The chicken fat, which was dark brown or black in color, was received *in gratis* from Tyson Foods in Scranton, Arkansas. In order to properly design each experiment and interpret laboratory data, molecular weights and relative concentrations of the components of the chicken fat were required. To estimate the molecular weight of triglycerides in the chicken fat, an average fatty acid containing triglyceride was used. The fatty acid composition of this triglyceride was determined using an average of reported fatty acid profiles of chicken fat. The chicken fat used consisted of approximately 12% free fatty acids (by mass), much greater than the chicken fat tested by Mattingly, which contained only 0.1 to 2.3% by mass.

The reaction products consisted of methyl esters (biodiesel), glycerol, water, and any unreacted methanol and chicken fat. The significant density difference between biodiesel and the glycerol/water layers was used to effect their separation.

1. The post-reaction reactor contents were placed into a 1000 mL separatory funnel, and allowed to sit for at least 12 hours.
2. The lower phase, which consisted of glycerol, water, and excess methanol, was decanted into a 400 mL beaker and weighed.
3. The upper phase, which consisted of biodiesel, excess methanol, and unreacted chicken fat, was decanted into another 500 mL beaker and weighed.

4. Both phases were distilled at 90° C for 60 minutes. The unreacted methanol was collected and weighed.
5. To remove any unreacted chicken fat from the biodiesel, 20-40 mL of deionized water were added to the biodiesel phase in another separatory funnel, mixed vigorously, and then allowed to settle for at least 12 hours.
6. The lower phase, consisting of unreacted chicken fat and water, was removed, followed by the upper phase, which consisted of refined biodiesel.
7. Finally, the final biodiesel was weighed and collected.

Results from the testing of chicken fat are discussed below. Note that the yield of biodiesel is defined and calculated as the mass percent of biodiesel recovered from the chicken fat charged to the reactor. It is notable that the maximum yield of biodiesel from chicken fat has a limit due to the glycerol that is formed.

The biodiesel produced from the supercritical reaction was easily separated from the methanol/glycerol/water layer, but retained the dark brown/black discoloration that the feed chicken fat possessed. In fact, the discoloration was so extreme the biodiesel was completely opaque, whereas a pale to dark yellow fuel was expected. In some instances there were solid particles present from the rendering facility, but these particles were easily removed with a wire-screen filter. After washing with warm water and mixing vigorously, the mixture separated into three distinct layers; biodiesel, unreacted chicken fat, and water (top to bottom). The unreacted chicken fat that was collected was lighter, and in some cases even pale yellow or white in color. Therefore, the contaminant that causes discoloration in the feed fat distributes preferentially with biodiesel, which is not unexpected due to biodiesel's solvating ability. From these findings, if the discoloration is unacceptable in the final fuel, the contaminants may be extracted before supercritical treatment. The optimal solvent and extraction conditions are beyond the scope of this study.

As can be seen in Figure 13, the yield of biodiesel from the chicken fat is greatly dependent upon the methanol to feed ratio. As the methanol to feed ratio was increased from 10:1 to 40:1, a dramatic increase in the biodiesel yield was observed for all temperatures tested. For instance, at a reaction temperature of 325°C and a methanol ratio of 10:1, a yield of only 31% was found. When the methanol ratio was increased to 40:1 however, the reaction was approximately complete giving a biodiesel yield of 89% (note that the maximum yield possible for a complete reaction was 91% due to the loss of the glycerol molecule).

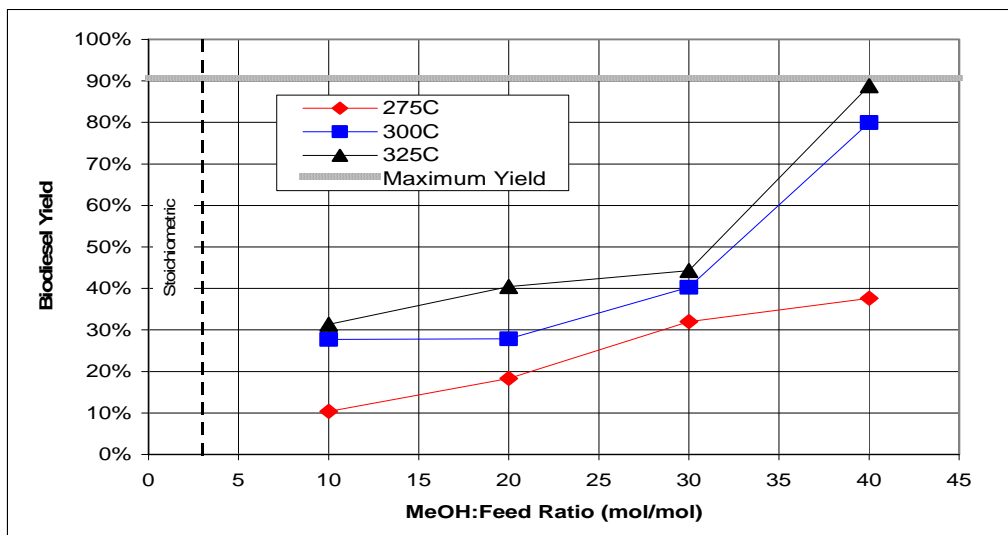


Figure 13. Results for the supercritical methanol treatment of chicken fat, 20 minute reaction time

For all temperatures tested, as the methanol ratio approached the theoretical minimum of 3:1, the biodiesel yield decreased rapidly. It is possible that the methanol acts as an acidic catalyst as suggested by other authors. If this were true, the conversion of chicken fat increased as the acid catalyst concentration was increased. These findings for the conversion of chicken fat compare favorably to those found with soybean or rapeseed oil in the literature, regardless of the poor quality of chicken fat used. This is notable since the yield characteristics for soybean- and rapeseed-derived biodiesel from supercritical methanol treatment are well known.

Important to note is that at all reaction temperatures tested, the yield of biodiesel was unacceptably low for tests with less than a 40:1 molar ratio of methanol to fat. Extrapolation of the data from this study suggest that at lower reaction temperatures, methanol ratios even greater than 40:1 would be required for sufficient conversion of chicken fat to biodiesel. To give perspective to weights and volumes required, Table 5 displays the conversions to a mass and volume ratio of methanol.

Table 5. Results from Supercritical Treatment of Chicken Fat

| Methanol/Chicken Fat Ratio | | | Biodiesel Yield | | |
|----------------------------|-----------|---------------|-----------------|--------|--------|
| mole/mole | mass/mass | volume/volume | 275°C | 300°C | 325°C |
| 10 | 0.657 | 0.720 | 10.38% | 27.71% | 31.37% |
| 20 | 1.314 | 1.439 | 18.33% | 27.88% | 40.43% |
| 30 | 1.971 | 2.159 | 32.02% | 40.30% | 44.30% |
| 40 | 2.628 | 2.879 | 37.61% | 79.97% | 88.87% |

The effect of temperature on the biodiesel yield from chicken fat can also be observed in Figure 14. At 275°C ($T_r = 1.07$), the lowest temperature investigated, low yields were obtained ranging from 10-38% based on the excess methanol used. When the temperature was raised to 300°C ($T_r = 1.12$), the yield increased significantly, ranging

from 28-80%. As expected, the greatest yields were obtained at 325°C ($T_r = 1.17$), the highest temperature tested, ranging from 31-89%.

A possible explanation for the low conversions observed at 275°C is the presence of multiple phases, due to the instability of the supercritical state. Using a supercritical reaction system with an equipped view-cell, Brignole, et al. visually determined conditions necessary for the formation of a single fluid phase⁷³. It was illustrated that, depending on the feed oil, a vapor/liquid two phase system can still exist up to a temperature of 290°C and pressure of 1,600 psia. There was also a strong correlation between single-phase formation and biodiesel yield. Though no view-cell was available in this study, it is a fair assumption, based on the results here and of the Brignole study that the chicken fat, water, and methanol at 275°C and 1,650 psia exist within two phases, possibly causing the poor extent of reaction. Figure 14 provides possible evidence for this explanation as the incremental increase in biodiesel yield between 275°C and 300°C (subject to phase and temperature differences) is generally greater than that between 300°C and 325°C (subject to temperature differences only).

Also, due to deficiencies in the equation of state model used to charge the reactor, at 275°C the pressure consistently reached by the system was approximately 1,300-1,400 psia for methanol ratios of 40, 30 and 20:1. For the 10:1 methanol ratio, however, the pressure reached only 1,095 psia, which is below the critical pressure of methanol. However, based on data in the literature, pressure differences at this scale should not drastically affect the yield of biodiesel, as two phases are already present in the mixture. Successful tests at 300°C and 325°C (pressure reached ~1,650 psia) confirm that higher yields are obtained at higher reaction temperatures. This is easily seen in Figure 14. At these conditions, Brignole et al. have visually confirmed a single fluid phase.

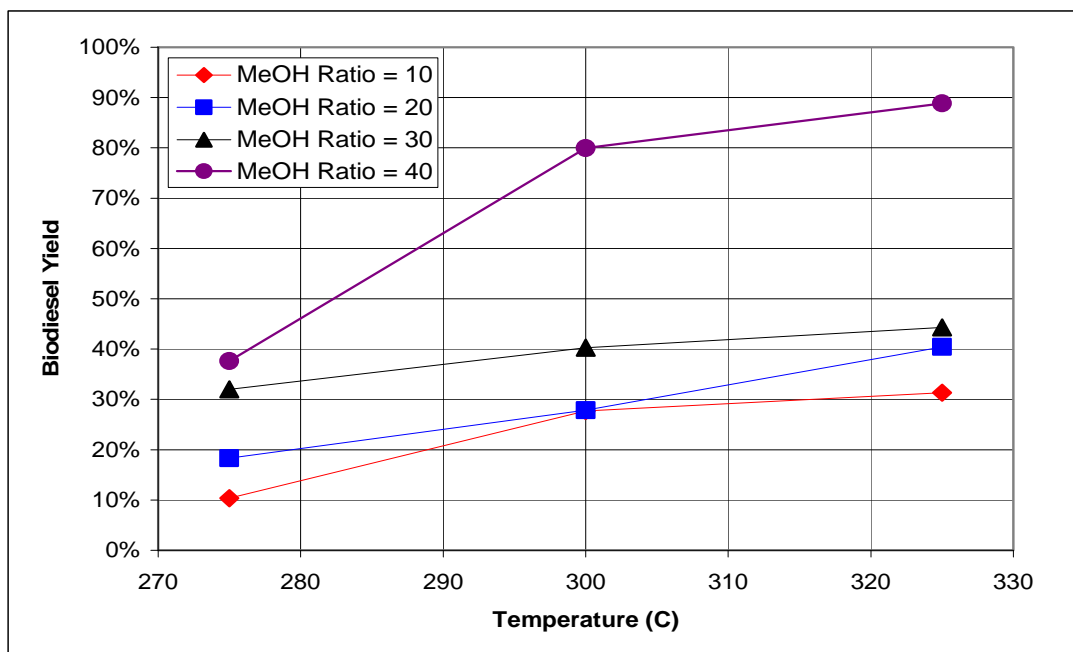


Figure 14. Results for the supercritical methanol treatment of chicken fat, 20 minute reaction time

Supercritical Methanol Treatment of Tall Oil Fatty Acids

According to the *Chemical Market Reporter*, essentially all of the crude tall oil produced in the United States undergoes fractionation into the five products. The tall oil fatty acid fraction is best suited for supercritical methanol treatment for biodiesel production. Therefore, one purpose of this study was to test tall oil fatty acids to determine the effect of reaction temperature and methanol to oil ratio and to determine conditions for the greatest yield of biodiesel.

The tall oil fatty acid sample used in this study (XTOL-100) was received in gratis from Georgia Pacific, in Crossett, Arkansas. While relative amounts of free fatty acids, resin acids, and unsaponifiables in crude tall oil have been shown to vary by location and type of tree, the fatty acids themselves are generally similar to those derived from animal and vegetable oils, containing mostly of C₁₈ compounds with small amounts of C₁₆, C₁₇, and C₂₀ acids. Sufficient for experimental design purposes, the fatty acid composition of a typical Southeastern U.S., < 2% resin acid-containing mixture of TOFA was assumed and is shown in Table 6. The small amounts of non-fatty acids were assumed to be abietic acid, the most common resin acid.

Table 6. Composition of tall oil fatty acids (Southeastern U.S.), adapted

| Compound | Mass Percent |
|--------------------|--------------|
| Palmitic acid | 0.4% |
| Palmitoleic acid | 0.7% |
| Stearic acid | 2.3% |
| Oleic acid | 46.0% |
| Linoleic acid | 46.2% |
| Eicosadienoic acid | 2.4% |
| Abietic Acid | 2.0% |

The supercritical treatment procedure used for tall oil fatty acids was very similar to that outlined for chicken fat. Considering the difference in feedstock type, however, the procedure for product separation and analysis was modified. The reactor products consisted of methyl esters (biodiesel), water, and any unreacted methanol and TOFA.

1. The post-reaction product mixture was placed in a separatory funnel. The lower phase, consisting of methanol and water was removed, followed by the upper phase, which consisted of biodiesel, excess methanol, and unreacted free fatty acids.
2. To remove methanol, the biodiesel phase was distilled at 90° C for 60 minutes. The unreacted methanol was collected and weighed.

- Any unreacted tall oil fatty acids in the biodiesel were titrated with a known amount of NaOH. Care was taken not to titrate the mixture beyond a pH of 8.5. This titration produced soaps from the saponification of free fatty acids.
- The soap and biodiesel mixture was centrifuged overnight.
- The lower or denser phase consisted of the soaps and water. This layer was removed.
- Finally, the final biodiesel, the upper or less dense phase, was weighed and collected.

Results from the testing of TOFA are discussed below. Note that the yield of biodiesel is defined and calculated as the mass percent of biodiesel recovered from the TOFA charged to the reactor. The biodiesel produced from the supercritical reaction was easily separated from the methanol/water layer, but unreacted tall oil fatty acids remained with the biodiesel, as indicated by a low pH (3-5). This mixture of TOFA and biodiesel was a translucent liquid with a darker yellow tint and a slight cloudiness for those tests that had lower conversions. For the reactions that were more complete, the biodiesel layer was a lighter shade of yellow that was completely translucent with no cloudiness.

The unreacted fatty acids were easily titrated with sodium hydroxide until the pH reached about 7.5-8. This left a thick and highly viscous soap slurry. After a few hours of centrifugation, however, the soap and final biodiesel layers were easily separated. As shown in Figure 15, it was found that the amount of methanol charged to the reactor also had a significant effect on the yield of biodiesel from tall oil fatty acids. As the methanol to feedstock oil ratio was increased from 10:1 to 40:1, a decrease in yield was observed. In fact, for each of the temperatures tested, there was approximately a 30% drop in biodiesel yield over the range of methanol ratios.

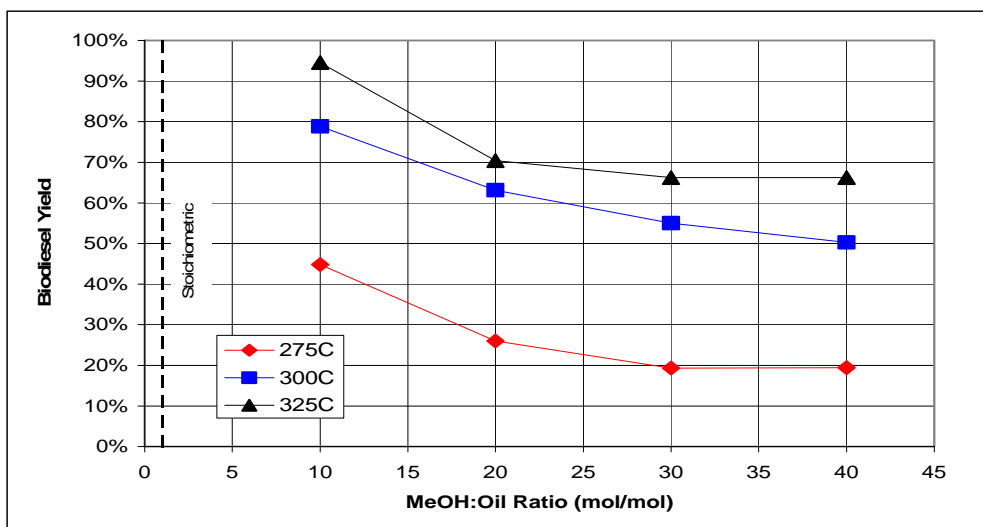


Figure 15. Results for the supercritical methanol treatment of TOFA (20 minute reaction time)

For instance, at 325°C, a yield of 94% was observed at a methanol ratio of 10:1, while at 40:1, the yield dropped to 66%. Though not indicated in the figure above, due to a mechanical failure in the cooling system, the 300°C, 30:1 run was allowed to react for

approximately 10 extra minutes (50% longer than others) before temperatures fell. This resulted in a presumably inflated yield of 55%. However, based on the remainder of the data, it can be estimated that the extraneous reaction time resulted in only 1-5% additional yield.

It is interesting to note that the biodiesel yield increased as the molar ratio of methanol approached the stoichiometric ratio, shown in Figure 15 to be 1:1. This was unexpected for a multitude of reasons. As the ratio is increased, there is an increased probability that a free fatty acid will make contact with a methanol molecule to support the esterification reaction. An increase in methanol concentration also helps repress the reverse hydrolysis reaction of biodiesel (methyl esters) and water to free fatty acid and methanol (see Figure 7). The results, however, do not support these known conventions. It is noteworthy that the relationship is much different than that found for chicken fat and the various triglyceride-based feedstocks tested in the literature. The significance of this difference will be addressed later.

It has been suggested by Minami and Saka in a very recent study (made available shortly after lab-work was completed) that free fatty acids present in the supercritical reaction mixture not only act as reactants, but also as acidic catalysts. Therefore, as the ratio of methanol to free fatty acids is increased, the relative concentration of the catalytic acid molecules is decreased. Results from testing with tall oil fatty acids in the present study defend this proposed reaction mechanism, as the yield of biodiesel decreases with increasing methanol to feed ratio. However, this trend does not continue for all higher molar ratios. As seen in Figure 15, beyond a ratio of 30:1, the effect of the methanol ratio on the yield of biodiesel is minimal for all the temperatures tested. This phenomena has not been explained in the literature, but might be attributed to the increased probability for methanol and free fatty acids to make contact to react, or the heightened effect of acid catalysis of methanol as with chicken fat conversion.

Table 7. Results from Supercritical Treatment of TOFA

| Methanol/TOFA Ratio | | | Biodiesel Yield | | |
|---------------------|-----------|---------------|-----------------|--------|--------|
| mole/mole | mass/mass | volume/volume | 275°C | 300°C | 325°C |
| 10 | 1.133 | 1.270 | 44.82% | 78.88% | 94.52% |
| 20 | 2.265 | 2.540 | 26.01% | 63.15% | 70.43% |
| 30 | 3.398 | 3.809 | 19.31% | 55.03% | 66.24% |
| 40 | 4.531 | 5.079 | 19.45% | 50.26% | 66.25% |

Effect of Temperature on TOFA Biodiesel Yield

The effect of temperature on the biodiesel yield from TOFA can also be seen in Figure 16. At 275°C ($T_r = 1.07$), the lowest temperature investigated, low yields were obtained ranging from 20-45% based on the excess methanol used. When the temperature was raised to 300°C ($T_r = 1.12$), the yield increased significantly, ranging from 50-80%. As expected, the greatest yields were obtained at 325°C ($T_r = 1.17$), the highest temperature tested, ranging from 65-98%. Based on these results, operating at a reaction temperature of 275°C is not suggested. The more soaps formed by titrating the unreacted TOFA made separation via centrifugation significantly more difficult.

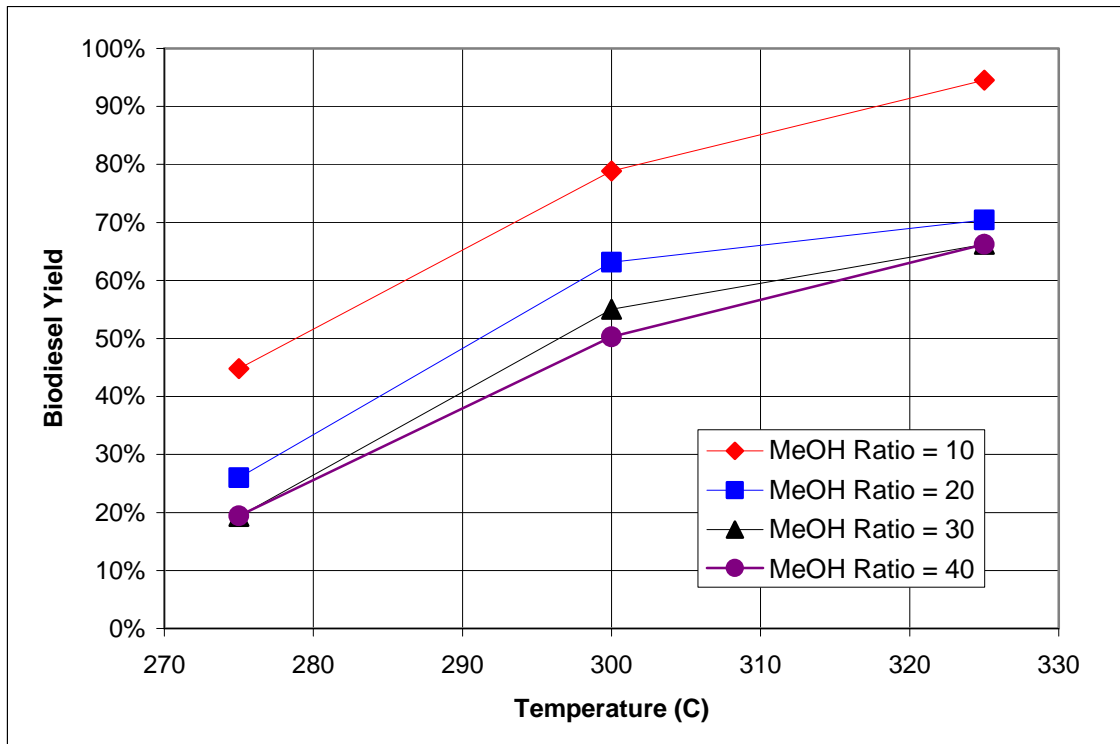


Figure 16. Results for the supercritical methanol treatment of TOFA, 20 minute reaction time

It is significant to note that increasing the temperature from 275-325° also had a diminishing return on the yield of biodiesel, as is better illustrated in Figure 16. For example, by increasing the reaction temperature for a 10:1 methanol ratio from 275°C to 300°C, a 35% rise in yield was observed. When further increased to 325°C, however, the yield increased by only 15%. This is very similar to test results from the supercritical treatment of chicken fat, which further supports the potentially important role of phase behavior in the supercritical reaction, as opposed to the effect of temperature alone.

Effect of Reaction Time on Biodiesel Yield

Due to the limitations of the batch reactor and heater system, the trials at temperatures of 300°C and 325°C were subjected to a 5 to 10 minute period (respectively) between 275°C and the target temperature. It is then plausible that the reactions may proceed during this transitory heating period, leading to some uncertainty in the reported yields. For this reason, another sample of tall oil fatty acids was treated with supercritical methanol at 300°C with a 10:1 methanol ratio. However, this sample was reacted for 60 minutes; three times that of those previously tested.

The biodiesel yield for a 60-minute supercritical methanol treatment of TOFA was found to be 83.6%, whereas that of the 20-minute treatment (all else equal) was 78.9%. Therefore, it has been shown that at 300°C, and at a 10:1 molar ratio of methanol to tall oil fatty acids, increasing the reaction time could increase the biodiesel yield. However, since the yield only increased by less than 5% after tripling the reaction time, it

is unlikely that there is much conversion of feedstock during the transitory heat-up period. The results also suggest that the reaction time might be optimized based on the yield and process throughput. Such optimization could increase productivity and decrease downstream processing requirements.

Conclusions for Tall Oil Fatty Acids & Chicken Fat Testing

Within the range of conditions tested in this study, essentially complete conversion of chicken fat and tall oil fatty acids was attained. A common observation between the two feedstocks is that higher temperatures resulted in higher yields. Also, for both feedstocks, the incremental increase in yield decreased with increasing temperature. The data of this study suggest a minimum temperature of approximately 325 C. The data suggest that the temperature should be minimized for process energy conservation as long as a single fluid phase under supercritical conditions is maintained during the reaction time. However, such optimization would require either 1) rigorous thermodynamic testing to develop effective phase modeling, or 2) visual confirmation of single-phase formation with a reactor equipped with a view cell.

Results from the supercritical treatment of these two feedstocks have also revealed an important difference. While the supercritical reactions with tall oil fatty acids were more complete with lower methanol ratios, the reactions with chicken fat were incomplete. Likewise, while the reactions with chicken fat were more complete with greater methanol ratios, the reactions with tall oil fatty acids were incomplete. Therefore, based on these results, the concentration of chicken fat (or triglycerides in general) should be kept below 27.5% by weight with methanol in a supercritical reaction for optimal conversion. The concentration of TOFA (or free fatty acids in general), on the other hand, should be kept above 47% by weight with methanol. These results compare favorably with studies involving other triglyceride- or free fatty acid-type feedstocks, as exemplified by Minami and Saka. This disjoint behavior suggests that a mixture of the two feedstocks cannot be completely converted in a single supercritical reaction in the 20 minute reaction time as used in this study, regardless of the temperature or the methanol to feed ratio tested.

Hydrolysis and Subsequent Supercritical Methanol Treatment

From an application standpoint, the conditions of the TOFA reaction are much more desirable. Not only were conversions for TOFA to biodiesel generally greater at each temperature tested in comparison to chicken fat (all else equal), but the amount of methanol required is much less, greatly decreasing costs associated with storing, heating, and recovering the reactant. As mentioned earlier, the hydrolysis of triglycerides results in the liberation of free fatty acids that can then be esterified. Considering the difference in optimal conditions for the chicken fat and the tall oil fatty acids, this two-step process appears to be a promising alternative to the single-step supercritical methanol treatment of a mixture of triglycerides and free fatty acids such as chicken fat and tall oil fatty acids. For this reason, this method was tested to convert a mixture of the two feedstocks.

A 50:50 mixture of tall oil fatty acids and chicken fat was hydrolyzed at 300°C and 1,240 psia using a 1:1 volumetric ratio of water to feedstock, conditions similar to those used by Minami and Saka. It is worth noting that this mixture of free fatty acids and triglycerides is similar to those found in other low-quality feedstocks being investigated for biodiesel production such as brown or yellow grease.

A 91.7% yield of free fatty acids was obtained from the feedstock mixture after the hydrolysis reaction (maximum of 95.5% possible). A large decrease in pH (6.3 to 2.6) and the formation of glycerol was observed. Following hydrolysis, the fatty acids were then esterified at 300°C and 1,650 psia using a methanol to feedstock ratio of 10:1 following the results from TOFA testing. A biodiesel yield of 82.3% was obtained from these free fatty acids, which is slightly higher than the yield obtained from the treatment of TOFA at these conditions (78.9%).

Results from the two-step hydrolysis and esterification of a mixture of chicken fat and tall oil fatty acids indicate that it is a successful pathway for producing biodiesel from triglyceride- and free fatty acid-containing feedstocks. This is particularly useful when considering mixtures of various low-quality materials.

Supercritical Methanol Treatment of Crude Tall Oil

While the yield results from the conversion of TOFA have shown to be promising, it still depends on a partially refined feedstock. Crude tall oil (CTO), from which TOFA is fractionated through distillation, is a much less expensive raw material, less than half the cost of the refined free fatty acids as seen in Figure 4. While the presence of resin acids and unsaponifiables is expected to yield undesirable cold flow properties after esterification, a sample of CTO was treated in supercritical methanol at 300°C and 1,650 psia, and with a 10:1 methanol to feed ratio.

Following supercritical treatment, a fuel yield of only 63.2% was obtained after titrating the unreacted acids. At the same conditions the yield from TOFA was 78.9%. It has been shown in the literature that rather stringent conditions are required for the esterification of resin acids such as those found in CTO due to steric hindrance. Therefore, it is likely that most of the unreacted acids that were saponified and removed were resinous in nature, accounting for the low yield obtained. On the other hand, it is expected that the unsaponifiables such as the sterols, aldehydes, and fatty alcohols present in the CTO remained in the fuel (organic phase) along with the newly formed resin esters.

Evaluation of Cold-Flow Properties

At lower temperatures, the high-molecular-weight compounds present in diesel fuels begin to solidify or gel, altering the physical properties of the fuel. For this reason, all diesel fuels are susceptible to start-up and performance problems when subjected to cold weather. Since biodiesel may contain long chain and high melting point compounds, poor cold flow properties of the fuel, such as a high viscosity or pour point, have been found. Dunn provides a comparison of biodiesel fuels derived from different feedstocks to illustrate how these cold flow properties depend heavily on the structure of

the feedstock used⁷⁴. For this reason, the viscosity and pour point of the fuels produced in this study were determined, as they must meet ASTM standards for use in the U.S.

The viscosity of each of the produced biodiesel fuels was measured with a calibrated Cannon-Fenske Routine viscometer. The procedure used was similar to that outlined in ASTM D445. Experimental efflux times are shown in Table 8 with the resulting kinematic viscosities of the fuels tested for comparison to known standards.

Table 8. Efflux time measurements for resulting fuels (40°C)

| Trial | Efflux Time (seconds) | | | |
|--------------------------------|-----------------------|----------------------------|--------------------------------|--------------------|
| | Biodiesel from TOFA | Biodiesel from Chicken Fat | Biodiesel from Feedstock Blend | Biodiesel from CTO |
| 1 | 1560.5 | 1870.0 | 1623.0 | 2654.0 |
| 2 | 1543.0 | 1894.0 | 1659.0 | 2615.5 |
| 3 | 1578.0 | 1862.0 | 1634.5 | 2597.0 |
| Average | 1560.5 | 1875.3 | 1638.8 | 2622.2 |
| Standard Deviation (%) | 1.12% | 0.89% | 1.12% | 1.11% |
| Viscosity (mm ² /s) | 6.162 | 7.406 | 6.472 | 10.355 |

It was found that all fuels had viscosities that were greater than that allowed by ASTM standards for neat (100%) biodiesel. The TOFA-derived biodiesel was approximately 2.7% greater than the maximum allowed whereas the chicken fat-derived biodiesel was 23% greater. The biodiesel produced from the mixed feed, as expected had a viscosity between these two pure feeds. Finally, the CTO-derived biodiesel had a very high viscosity, over 10 mm²/s, likely due to resin esters and unsaponifiables. In comparison to biodiesel produced from soybean oil in the conventional production process, for which viscosities up to 4.4 mm²/s have been reported, the viscosities determined in the current study are high. In a recent study of the acid catalyzed esterification of TOFA, the authors found the resulting methyl esters had an elevated viscosity (7.1 mm²/s) similar to that found in the current study (6.2)⁷⁵. The particular composition of fatty acids in the feedstock has been suggested to have a noticeable effect on the viscosity. It was also demonstrated that simple blending with petroleum diesel lowered the viscosities down to acceptable levels.

To meet ASTM standards for biodiesel however, the highest allowable viscosity before blending with diesel is 6.0 mm²/s. Results from this study suggest that blending with soybean oil-derived biodiesel (or from other fuels with acceptable viscosities) would be required for the methyl esters of tall oil & chicken fat to be classified as biodiesel in industry.

The cloud point of each of the produced biodiesel fuels was determined under the conditions described in ASTM D2500 (See Figure 9). While the opaque nature of the chicken fat- and CTO-derived fuels prevented any reliable cloud point determination, that of the TOFA-derived fuel was easily obtained. The TOFA-derived biodiesel was found to have a cloud point of 6°C. The ASTM D6751 does not regulate the cloud point temperature, but rather requires biodiesel sellers to disclose the property to any potential

buyers. For this reason, cloud points determined in this study were compared with soybean oil methyl esters from another study. As can be seen in Table 10, the cloud points of the fuels produced in this study are comparable to the soybean oil-derived biodiesel that is produced in industry today.

Table 9. Visual Descriptions for Cloud Point Measurements

| Temperature (°C) | Description | |
|------------------|-------------------------------|----------------------------|
| | Biodiesel from TOFA | Biodiesel from Chicken Fat |
| 23 | translucent, yellow tint | opaque, black |
| 22 | translucent, yellow tint | opaque, black |
| 21 | translucent, yellow tint | opaque, black |
| 20 | translucent, yellow tint | opaque, black |
| 19 | translucent, yellow tint | opaque, black |
| 18 | translucent, yellow tint | opaque, black |
| 17 | translucent, yellow tint | opaque, black |
| 16 | translucent, yellow tint | opaque, black |
| 15 | translucent, yellow tint | opaque, black |
| 14 | translucent, yellow tint | opaque, black |
| 13 | translucent, yellow tint | opaque, black |
| 12 | translucent, yellow tint | opaque, black |
| 11 | translucent, hazy (localized) | opaque, black |
| 10 | translucent, hazy (localized) | opaque, black |
| 9 | translucent, hazy (localized) | opaque, black |
| 8 | translucent, hazy | opaque, black |
| 7 | translucent, hazy | opaque, black |
| 6 | cloudy, (localized) | opaque, black |
| 5 | cloudy, (localized) | opaque, black |
| 4 | cloudy, (localized) | opaque, black |
| 3 | cloudy, (localized) | opaque, black |
| 2 | cloudy, (opaque) | opaque, black |
| 1 | cloudy, (opaque) | opaque, black |
| 0 | cloudy, (opaque) | opaque, black |
| -1 | cloudy, (opaque) | opaque, black |

Table 10. Viscosity and cloud point results and comparison with ASTM standards

| | #2 Diesel ASTM D975 | Biodiesel ASTM D6751 | Biodiesel Feedstock | | | | |
|--------------------------------|---------------------|----------------------|---------------------|------|---------------|------|-------------|
| | | | Chicken Fat | TOFA | CF/TOFA Blend | CTO | Soybean Oil |
| Viscosity (mm ² /s) | 1.9-4.1 | 1.9-6.0 | 7.4 | 6.2 | 6.5 | 10.4 | 4.4 |
| Cloud Point (°C) | -16 | Report | N/A | 6 | N/A | N/A | 3 |

The cold flow properties of neat tall oil fatty acid methyl esters and chicken fat methyl esters have failed to meet standards, as have blends of the two. While the cloud point and discoloration are negotiable with the buyer, the high viscosities would prohibit titling the methyl esters "biodiesel" under ASTM D6751, especially those from the crude tall oil. A biodiesel plant intending to use these feedstocks would need to either produce soybean oil methyl esters or have access to them for blending in order to meet the ASTM specifications.

A study of the marginal costs associated with the incremental increase/decrease of methanol to feed ratio and temperature is required to determine the optimal reaction conditions. By accounting for the increased pumping, heating, and/or recovery costs with respect to the biodiesel yield at these various conditions, the optimal temperature and methanol ratio could be determined.

Safety Considerations

For all work conducted in the laboratory, standard personal protective equipment was worn to decrease potential areas of contact with the materials involved, particularly methanol. This included but was not limited to long pants, safety glasses, impervious gloves, and closed-toe shoes. However, the high temperatures and pressures required for supercritical methanol treatment, not to mention the flammability and toxicity of methanol (See Table 11), warranted some special process safety considerations. The reactor location, contents, and testing conditions were carefully selected to provide a safe working environment during testing. The stirred-tank reactor was placed outdoors on a concrete slab approximately 15-20 feet from laboratory room 131 in the University of Arkansas Engineering Research Center, from which observation took place. A semicircle shield constructed from three slabs of ½" thick, 3'x 5' reinforced cement-board supported by sand bags was placed 1 foot away from the reactor. This location provided a well-ventilated area in the case of an incidental release of toxic or flammable methanol vapors.

Table 11. Flammability and toxicity data for methanol

| | |
|---|---|
| Flash point | 11°C |
| Limiting oxygen concentration (LOC)⁷⁶ | 12% (by volume) |
| Toxicity Data | Toxic by inhalation, skin contact, or ingestion. OSHA TWA: 200 ppm |
| Upper flammability limit (UFL) | 36% (by volume) |
| Lower flammability limit (LFL) | 6% (by volume) |
| Auto-ignition temperature | 464°C |

Conversely, ventilation in a standard laboratory hood may be insufficient, resulting in a dangerous cloud of toxic and flammable vapor. Thus the outdoors location of the reactor acted to minimize any potential damage to personnel and/or the building due to toxicity or the unlikely chance of ignition. The semi-circle arrangement of the cement shield allowed further protection by focusing any potential release or blast away from the building and personnel. A fire extinguisher was located in the lab in case of an emergency. Finally, a minimum of 2 laboratory personnel was present on location for each experiment.

Since methanol has such a low flash point (11°C), any oxygen present in the reactor was removed via pressure purging to concentrations below its limiting oxygen concentration (12% by volume). Carbon dioxide was chosen as an inerting agent, as it has also been shown to be a good co-solvent for the system. Four purges with carbon dioxide at 100 psig resulted in an oxygen concentration of approximately 98.1 parts per million ($9.5 \times 10^{-3} \%$), well below the 12% LOC for methanol.

To minimize the amount of flammable methanol required, deionized water was added to the reactor. Previous studies have shown that the presence of water in the reaction mixture, at least up to a 1:1 mass ratio with the feedstock, does not affect the yield of biodiesel. The addition of water also serves to simulate the use of various low-quality feedstocks that may have high moisture contents. The presence of water also makes product separation easier. Based on these findings, a mass of water equal to that of the sample was used, decreasing the sample and methanol requirements by up to 60%.

As mentioned earlier, the pressure vessel used in this study was rated at 1,900 psia at 350°C. It was anchored to the heater that was anchored to the concrete slab, preventing it from becoming a projectile in case of a release or explosion. All experiments were carried out at a maximum of 1,650 psia and 325°C, which were sufficiently below the vessel's rating while still well above the critical conditions of methanol. The experimental conditions were well below the maximum allowed by the

burst disc that was installed, rated at 2,000 psia, which provided safety relief in the case of over-pressurization. There were one-foot segments of stainless steel tubing directed away from the building and personnel that served as vent lines from both the pressure relief device and gas release valve.

Safety concerns during the preparatory work within the laboratory were also considered. Any transfer of methanol was conducted within a laboratory hood with proper ventilation, and any large transfers were conducted under proper electrically grounded conditions. This prevented the generation of any spark during the transfer that could ignite the methanol. Safety equipment such as an eyewash station, safety shower, first aid kit, and spill kit should be readily available.

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