

BIODIESEL PRODUCTION FROM OILS AND FATS WITH HIGH FREE FATTY ACIDS

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ABSTRACT. Biodiesel is an alternative fuel for diesel engines consisting of the alkyl monoesters of fatty acids from vegetable oils or animal fats. Most of the biodiesel that is currently made uses soybean oil, methanol, and an alkaline catalyst. The high value of soybean oil as a food product makes production of a cost-effective fuel very challenging. However, there are large amounts of low-cost oils and fats such as restaurant waste and animal fats that could be converted to biodiesel. The problem with processing these low cost oils and fats is that they often contain large amounts of free fatty acids (FFA) that cannot be converted to biodiesel using an alkaline catalyst. In this study, a technique is described to reduce the free fatty acids content of these feedstocks using an acid-catalyzed pretreatment to esterify the free fatty acids before transesterifying the triglycerides with an alkaline catalyst to complete the reaction. Initial process development was performed with synthetic mixtures containing 20% and 40% free fatty acids, prepared using palmitic acid. Process parameters such as the molar ratio of alcohol, type of alcohol, acid catalyst amount, reaction time, and free fatty acids level were investigated to determine the best strategy for converting the free fatty acids to usable esters. The work showed that the acid level of the high free fatty acids feedstocks could be reduced to less than 1% with a 2-step pretreatment reaction. The reaction mixture was allowed to settle between steps so that the water-containing alcohol phase could be removed. The 2-step pretreatment reaction was demonstrated with actual feedstocks, including yellow grease with 12% free fatty acids and brown grease with 33% free fatty acids. After reducing the acid levels of these feedstocks to less than 1%, the transesterification reaction was completed with an alkaline catalyst to produce fuel-grade biodiesel.

Keywords. Alternative fuel, Biodiesel, Diesel, High free fatty acid, Rendered animal fat, Waste restaurant oil.

Throughout its history, the diesel engine has been the subject of a great deal of research and development. This work has focused on improving emissions and fuel economy and, more recently, on finding an appropriate fuel. For many years, the ready availability of inexpensive middle-distillate petroleum fuels provided little incentive for experimenting with alternative, renewable fuels for diesel engines. However, since the oil crisis of the 1970s, research interest has expanded in the area of alternative fuels. Many proposals have been made regarding the availability and practicality of an environmentally sound fuel that could be domestically sourced. Methanol, ethanol, compressed natural gas (CNG), liquefied petroleum gas (LPG), liquefied natural gas (LNG), vegetable oils, reformulated gasoline, and reformulated diesel fuel have all been considered as alternative fuels. Of these alternative fuels, only ethanol and vegetable oils are non-fossil fuels.

Many researchers have concluded that vegetable oils hold promise as alternative fuels for diesel engines (Goering et al., 1982; Bagby et al., 1987). However, using raw vegetable oils

for diesel engines can cause numerous engine-related problems (Korus et al., 1982; Van der Walt and Hugo, 1982). The increased viscosity and low volatility of vegetable oils lead to severe engine deposits, injector coking, and piston ring sticking (Vellguth, 1983; Clark et al., 1984; Pestes and Stanislao, 1984; Perkins and Peterson, 1991). However, these effects can be reduced or eliminated through transesterification of vegetable oil to form methyl esters, commonly known as *biodiesel* (Zhang et al., 1988; Perkins and Peterson, 1991). Transesterification provides a fuel viscosity that is close to that of No. 2 diesel fuel.

Biodiesel is receiving increased attention as an alternative, non-toxic, biodegradable, and renewable diesel fuel. Its properties vary somewhat depending on the oil feedstock and alcohol used but it can always be used as a direct substitute for diesel fuel (Mittelbach et al., 1992; Peterson et al., 1992; Peterson et al., 1994). Biodiesel has a higher cetane number than diesel fuel, no aromatics, almost no sulfur, and contains 10% to 11% oxygen by weight. These characteristics of biodiesel reduce the emissions of carbon monoxide (CO), hydrocarbon (HC), and particulate matter (PM) in the exhaust gas compared to petroleum-based diesel fuel. In spite of its desirable properties as a diesel fuel substitute, biodiesel from food-grade oils is not economically competitive with petroleum-based diesel fuel. Lower-cost feedstocks are needed. The objective of this study was to develop a process for producing fuel quality biodiesel from low-cost feedstocks with high FFAs. The process development is described in this article and the implementation of the process on a pilot plant scale is described in a second article (Canakci and Van Ger-

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pen, 2001). This second article also contains an economic analysis of the process.

Waste oils and fats are currently collected from large food processing and service facilities where they are rendered and used primarily in animal feed. Rendered animal fats and restaurant waste oils with free fatty acid levels of less than 15% are known as *yellow grease*. If the FFA level exceeds 15%, it may be sold at a discount as *brown grease*, or blended with low FFA material to meet the yellow grease specifications. The price of yellow grease varies widely from \$0.09–\$0.20/lb (Rudbeck, 2000). Brown grease is usually discounted \$0.01–\$0.03/lb below this amount (Simonsen, 2000). Yellow and brown grease are attractive feedstocks for biodiesel production because they are inexpensive compared with food-grade vegetable oil. There are large amounts of waste vegetable oils from the food industry that could be converted to biodiesel. Approximately 2.5 billion pounds of waste restaurant greases are collected annually from restaurants and fast-food establishments in the United States (Hauermann, 1990).

Oils and fats are composed primarily of triglycerides. Triglycerides consist of a glycerin backbone with fatty acid radicals attached in place of the hydroxyls. The relative amounts of the different fatty acid radicals determine the properties of the specific triglyceride. Table 1 shows the fatty acid distribution of some common vegetable oils and animal fats. Saturated compounds (C14:0, myristic acid; C16:0, palmitic acid; C18:0, stearic acid) have higher cetane numbers and are less prone to oxidation than unsaturated compounds but they tend to crystallize at unacceptably high temperatures.

A number of researchers have worked with feedstocks that have elevated FFA levels (Freedman et al., 1984; Mittelbach and Tritthart, 1988; Mittelbach et al., 1992; Peterson et al., 1995; Wimmer, 1995). However, in most cases, alkaline catalysts have been used and the FFAs were removed from the process stream as soap and considered waste.

As FFA levels increase this becomes undesirable because of the loss of feedstock as well as the deleterious effect of soap on glycerin separation. The soaps promote the formation of stable emulsions that prevent separation of the biodiesel from the glycerin during processing.

Waste greases typically contain from 10% to 25% FFAs. This is far beyond the level that can be converted to biodiesel using an alkaline catalyst. An alternative process is to use acid catalysts that some researchers have claimed are more tolerant of free fatty acids (Freedman and Pryde, 1982; Aksoy et al., 1988; Liu, 1994). Previous work has indicated that acid catalysts are too slow to be practical for converting triglycerides to biodiesel (Canakci and Van Gerpen, 1999). However,

acid catalysts appear to be quite effective at converting FFAs to esters and this reaction is fast enough to be practical (Jeromin, 1987; Hammond, 1998). Thus, an acid-catalyzed pretreatment step to convert the FFAs to esters followed by an alkali-catalyzed step to convert the triglycerides should provide an effective and efficient method to convert high FFA feedstocks to biodiesel. A search of the patent literature showed that others had taken advantage of this approach (Kawahara et al., 1979; Lepper et al., 1986; Stern et al., 1987).

Freedman and Pryde (1982), Liu (1994), and Mittelbach et al. (1992) have mentioned that the oil should not contain more than 1% FFA for alkaline-catalyzed transesterification reactions. This corresponds to an acid value of 2 mg KOH/g. If the FFA level exceeds this amount, the formation of soap will inhibit the separation of the ester from the glycerin and also reduce the ester conversion rate. Work to be presented later shows that this limit should be 1 mg KOH/g (0.5% FFA) for at least one alkaline catalyst, and this is supported by other researchers (Feuge et al., 1945; Nye and Southwell, 1984). However, the work presented here is based on the initial assumption that the acid catalysis must decrease the acid value of the mixture to less than 2 mg KOH/g.

The other major obstacle to acid-catalyzed esterification for FFAs is water formation. Water can prevent the conversion reaction of FFAs to esters from going to completion. Keim et al. (1945) patented a process for esterification of oils containing over 50% free fatty acids. In a case study described in the patent, unbleached palm oil containing 50.8% free fatty acids was mixed with methanol (77% of the weight of the oil) and sulfuric acid (0.75% of the weight of the oil) and stirred at 69°C for 1 h. The reaction products were distilled under vacuum and the yield obtained was 97.0%. The acid value of the distillate was equivalent to about 5% palmitic acid. This acid level is approximately equal to an acid value of 10 mg KOH/g which is much higher than the value of 0.8 mg KOH/g specified in ASTM specification PS121 for biodiesel (Howell, 1997). The water created by the acid-catalyzed reaction of the FFAs with the methanol probably stopped the esterification reaction before it could be completed.

In a previous study (Canakci and Van Gerpen, 1999), the relationship between FFA level and triglyceride conversion was investigated. Sample mixtures were prepared by adding palmitic acid to soybean oil to obtain free fatty acid levels between 5% and 33%. The conversion rate of soybean oil to methyl ester dropped from 90.54% to 58.77% as the FFA level increased from 5% to 33%. It will be shown later that water formed by the reaction was responsible for halting the reaction.

Table 1. Fatty acid distribution of some vegetable oils and animal fats.

Product	Fatty acid distribution (% by weight)							Saturation level (%)	Reference
	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3		
Rapeseed oil	–	3.49	–	0.85	64.40	22.30	8.23	4.34	Goering, 1982
Sunflower oil	–	6.08	–	3.26	16.93	73.73	–	9.34	Goering, 1982
Safflower oil	–	8.60	–	1.93	11.58	77.89	–	10.53	Goering, 1982
Soybean oil	–	10.58	–	4.76	22.52	52.34	8.19	15.34	[a]
Lard	1–2	28–30	–	12–18	40–50	7–13	–	41–50	Linstromberg, 1970
Tallow	3–6	24–32	–	20–25	37–43	2–3	–	47–63	Linstromberg, 1970
Yellow grease	2.43	23.24	3.79	12.96	44.32	6.97	0.67	38.63	[a]
Brown grease	1.66	22.83	3.13	12.54	42.36	12.09	0.82	37.03	[a]

[a] Measured by Woodson–Tenent Laboratories, Inc., Des Moines, Iowa.

EXPERIMENTAL METHODS

The objective of this study was to develop a technique for producing fuel-grade biodiesel from low-cost feedstocks. The project was divided into two specific tasks:

- Develop a technique to reduce the FFA level of high FFA feedstocks to less than 1% FFA with an acid-catalyzed pretreatment.
- Optimize the use of an alkaline catalyst to complete the reaction and produce fuel grade biodiesel.

To investigate the effects of molar ratio, reaction temperature, reaction time, and catalyst amount on the acid-catalyzed conversion of free fatty acids to methyl esters, a laboratory-scale reactor was used. The reactor consisted of a 1000 cc glass flask and a water-cooled condenser that returned any vaporized methanol to the reacting mixture. Unless otherwise noted, the reaction temperature was maintained at 60°C using a hot plate. This temperature was below the boiling point of methanol so the reaction vessel did not need to be pressurized. The mixture was stirred at the same rate for all runs. The same setup was also used for the alkaline-catalyzed transesterification tests although those tests were at room temperature. This system had been used previously for initial investigations of acid-catalyzed transesterification (Canakci and Van Gerpen, 1999). The progress of the reaction was monitored by measuring the elimination of the FFAs using American Oil Chemists' Society Official Method Cd 3a-63 for Acid Value (AOCS, 1998) and the residual glycerin using Official Method Ca 14-56 (AOCS, 1991).

RESULTS AND DISCUSSION

PREPARATION OF METHYL ESTER FROM MATERIAL WITH HIGH FFA

This section describes a series of tests that were conducted to develop the acid-catalyzed pretreatment process. Since animal fat tends to have variable properties that could influence the repeatability of the tests, a simulated animal fat was prepared by adding 20% and 40% palmitic acid (by weight) to soybean oil. The initial acid value of the soybean oil was measured to be 0.10 mg KOH/g. After palmitic acid addition, the acid value increased to 41.33 and 91.73 mg KOH/g for 20% and 40% palmitic acid, respectively. These are the initial values of acid value shown in the tables and figures that follow. Palmitic acid was chosen because it is one of the dominant fatty acids present in most vegetable oils and animal fats and it is available at relatively low cost.

PROCESS DEVELOPMENT

Published results suggested that the acid catalysis must decrease the acid value of the mixture to less than 2 mg KOH/g before the alkaline catalysis will give satisfactory results, and this was the initial target for the pretreatment (Freedman and Pryde, 1982; Mittelbach et al., 1992; Liu, 1994; Canakci and Van Gerpen, 1999). Previous work (Canakci and Van Gerpen, 1999) showed that the acid-catalyzed reaction stops in many cases at an acid value that is well above the 2 mg KOH/g target. This is due to the effect of the water produced when the FFAs react with the alcohol to form esters. Figure 1 from the previous study (Canakci and Van Gerpen, 1999) shows a comparison between the ester conversion when water is produced by FFA conversion and when water is

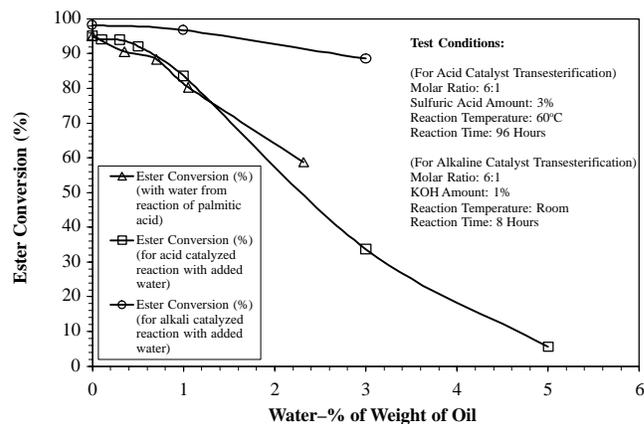


Figure 1. Comparison of the FFA and water addition tests.

deliberately added to soybean oil. The coincidence of the lines indicates that water formation is the primary mechanism limiting the completion of the esterification reaction with FFAs.

Effect of Catalyst Amount and Reaction Time on the Acid Value of the Synthetic Mixture

To investigate the influence of catalyst amount and reaction time on the acid value of the vegetable oil with 20% and 40% palmitic acid, four different sulfuric acid amounts (0, 5, 15, and 25 wt% of the FFA) and a 1-h reaction time were selected. After the initial mixing of the reactants, samples were extracted at 1 min, 15 min, 30 min, and 60 min, and the acid value was measured. The acid values of the original vegetable oil and the vegetable oil/palmitic acid mixture before the methanol was added were also recorded. All samples from the test with zero catalyst were solid at room temperature and required heating to measure the acid value. After 1 h, the reacting mixture was allowed to settle. A methanol-water mixture separated from the oil phase at the top of the separatory funnel for the 5 wt% catalyst amount test. However, for the 15 and 25 wt% catalyst tests the methanol-water mixture was found at the bottom of the funnel.

The influence of the catalyst amount on the acid value during the 1-h test, is shown in table 2 for a 9:1 molar ratio of methanol to FFA. As can be seen, with zero catalyst the acid value reached only 33.38 mg KOH/g at the end of the test. However, with the catalyst present, there was a very rapid reduction in acid value that occurred immediately after addition of the methanol-sulfuric acid solution to the oil-FFA mixture. The acid value of the 20% palmitic acid mixture was reduced from 41.33 to 1.77 mg KOH/g when 5% sulfuric acid catalyst was used. When the catalyst level was increased to 25%, the acid value decreased to 0.54 mg KOH/g. For the 40% palmitic acid case, the acid value decreased from 91.73 to as low as 6.25 mg KOH/g. However, even when 25% H₂SO₄ was used, the acid value did not reach the 2 mg KOH/g target.

Effect of Alcohol Type

To investigate the effect of a different alcohol type on the acid value reduction, ethanol was tested at the same conditions used previously for methanol, except that the reaction temperature was raised to 75°C, a few degrees below the boiling point of ethanol. The ethanol to FFA molar ratio was 9:1 and the sulfuric acid catalyst amounts were 5%, 15%, and

Table 2. Effect of catalyst amount and reaction time on the acid value of soybean oil containing 20% and 40% palmitic acid^[a].

Run time (hours)	Acid value (mg KOH/g)						
	20% FFA			40% FFA			
	Catalyst amount				Catalyst amount		
	0%	5%	15%	25%	5%	15%	25%
0 hours	0.10	0.10	0.10	0.10	0.10	0.10	0.10
0 hours (after palmitic acid addition)	41.33	41.33	41.33	41.33	91.73	91.73	91.73
One minute after catalyst addition	38.19	13.66	13.44	14.45	27.89	23.52	37.52
0.25	37.07	5.80	2.86	4.30	22.40	19.15	21.06
0.50	35.73	3.83	1.15	0.92	21.84	14.11	13.17
1.00	33.38	1.77	0.67	0.54	18.82	8.09	6.25

^[a] 9:1 molar ratio of methanol to FFA; catalyst: H₂SO₄.

25%, based on the FFA weight in the mixture, for a 1-h reaction time. The test results are shown in table 3. The minimum acid value for the 20% FFA case, after 1 h, was measured to be 3.00 mg KOH/g with 25% sulfuric acid. While the final acid values for the 20% FFA case were higher for ethanol than for methanol, the rate of the reaction was faster for ethanol. This may be due to the higher reaction temperature or ethanol's higher solubility in oils and esters. The final acid values for ethanol reacting with the 40% FFA feedstock were lower than with methanol. Another observation was that the samples taken in the tests with ethanol did not freeze while being stored in the refrigerator, as was observed for the tests with methanol.

DEVELOPMENT OF 2-STEP PRETREATMENT PROCESS

The tests described above show that the FFA level of the 20% FFA synthetic mixture can be decreased to below the target of 1% (2 mg KOH/g). However, the amounts of catalyst and methanol were considered to be quite high, and FFA levels of 40% could not be processed. A method that would be sufficiently robust to process 40% FFA mixtures while using reasonable amounts of methanol and acid was needed. Since water formation when the FFAs are converted to esters inhibits the reaction, the water must be removed to complete the reaction. Hammond (1998) suggested that this could be

Table 3. Effect of ethanol on acid value for 20% and 40% palmitic acid test^[a].

Run time (hours)	Acid value (mg KOH/g)					
	20% FFA			40% FFA		
	Catalyst amount			Catalyst amount		
	5%	15%	25%	5%	15%	25%
0 hours	0.10	0.10	0.10	0.10	0.10	0.10
0 hours (after palmitic acid addition)	41.33	41.33	41.33	91.73	91.73	91.73
One minute after catalyst addition	4.14	4.19	3.35	8.96	6.92	7.80
0.25	4.17	3.58	2.46	9.18	7.15	5.35
0.50	3.79	3.50	2.73	8.89	5.49	6.61
1.00	3.63	3.57	3.00	8.09	5.60	6.45

^[a] 9:1 molar ratio of ethanol to FFA; catalyst: H₂SO₄.

accomplished using a multi-step process. The first step would be conducted as previously described. When the reaction has reached equilibrium after 15 min to 1 h, the mixture would be allowed to settle and the methanol-water fraction that separates would be removed. Then, additional methanol and acid catalyst can be added and the reaction continued for another step. Although experience has shown that only two steps are usually needed, this sequence can be repeated as many times as necessary to reduce the acid level below 1%. This two-step acid-catalysis process offers the potential to reach lower FFA levels while using less alcohol and catalyst. The effect of molar ratio, reaction time, and acid catalyst amount on the acid value of the mixture was determined for a 2-step reaction at 60° C. Initially, a two-step pretreatment process was investigated with each reaction. Thirty minutes were allowed so that the total reaction time would be the same as the single-step pretreatment. While it was found to be possible to accomplish the pretreatment with two 30-min pretreatment steps, it was clear that the amount of sulfuric acid and methanol could be substantially reduced if the time for each step were extended to 60 minutes.

With a 1-h reaction time for the first step and a 10:1 molar ratio of methanol, the acid value of the 20% palmitic acid mixture decreased to 2.87 mg KOH/g. Using the product from this first step, and a reaction time of 1 h, the molar ratio for the second step was varied from 6:1 to 35:1. The acid value of the mixture decreased to less than 2 mg KOH/g even with the lowest molar ratio used in the second step as can be seen in figure 2. This approach appeared to provide a robust process that could achieve the targeted acid value with sufficient margin to allow for property variations in the feedstock.

Effect of Acid Value on Alkaline-Catalyzed Transesterification

After the acid value of the high FFA oil was reduced to less than 2 mg KOH/g with the 2-step pretreatment, the reaction was continued with alkaline-catalyzed transesterification. A test case of alkaline-catalyzed transesterification was run using a pretreated sample that had an acid value of 1.86 mg KOH/g. A 6:1 molar ratio of methanol and 1% alkaline catalyst (KOH) were used based on the amount of unreacted oil in the mixture. However, the total glycerin amount in the final product was measured to be 0.29% using the American Oil Chemists' Society official test method known as the Total,

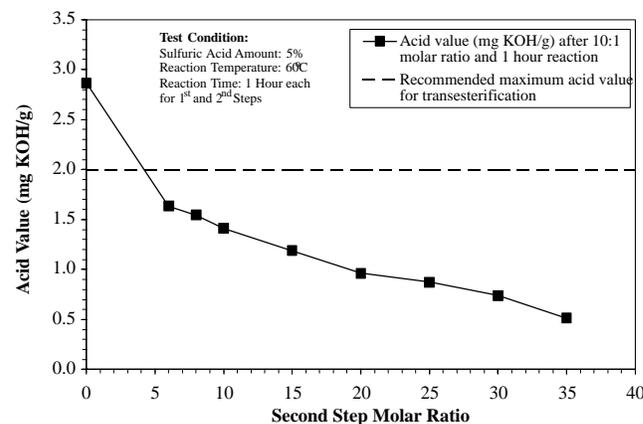


Figure 2. Effect of molar ratio on the acid value of the mixture in 2nd step for 1 h reaction time.

Table 4. Fatty acid composition of the yellow grease and soybean oil.

Product	Carbon chain (% by wt.) ^[a]										Unknown components	Sat. (% by wt.)
	C14:0	C15:0	C16:0	C16:1	C17:0	C18:0	C18:1	C18:2	C18:3	C20:0		
Soybean oil	–	–	10.29	–	0.11	4.28	21.55	53.68	8.16	0.34	0.91	15.22
Yellow grease	1.73	0.23	21.75	4.45	0.56	12.05	40.61	11.03	1.38	0.19	1.39	36.51

^[a] Measured by Woodson–Tenent Laboratories, Inc., Des Moines, Iowa.

Free, and Combined Glycerol (Iodometric–Periodic Acid) Method (AOCS, 1991). This total glycerin amount was too high to meet the total glycerin specification. A series of tests conducted with various FFA levels found that with KOH as the catalyst, the FFA level must be less than 1 mg KOH/g in order to produce ester with less than 0.24% total glycerin. The results of other researchers (Feuge and Gros, 1949; Freedman et al., 1984) confirm these results. Results to be reported later show that sodium methoxide is more tolerant of FFAs than KOH.

PREPARATION OF METHYL ESTERS FROM YELLOW AND BROWN GREASE

To determine whether the process developed using the synthetic high FFA feedstock could be extended to actual feedstocks, methyl esters of yellow and brown grease were prepared. The yellow grease was obtained from the Simonsen rendering plant in Quimby, Iowa. Rendering plant greases typically have a FFA level between 5% and 25% depending on the time of year. The specific fat analyzed for this project had an acid value of 25.15 mg KOH/g, which corresponds to a FFA level of about 12%. The fatty acid distribution of the yellow grease is shown in table 4 compared to soybean oil. As would be expected from yellow grease derived primarily from animal fat, the fat was solid at room temperature.

Pretreatment of Yellow and Brown Grease

After filtering the yellow grease at 55–60°C using a 105 µm mesh polypropylene filter, a 5% sulfuric acid solution with a 7.4:1 molar ratio of methanol to FFA, was added. The reaction was continued for 30 minutes at 60°C. After settling overnight and separating the methanol–water mixture from the top, the acid value of the fat–ester mixture was measured to be 14.63 mg KOH/g. This value was much higher than was expected based on the work described earlier with the synthetic high FFA mixtures. The acid value change of the synthetic mixture with 20% palmitic acid decreased from 41.33 mg KOH/g to 8.31 mg KOH/g with an 7.4:1 molar ratio while the yellow grease which started at 25.15 mg KOH/g only decreased to 14.63 mg KOH/g. A number of possible reasons for the difference were proposed. Initially, it was thought that the water in the yellow grease could be inhibiting the reaction. However, the water formed in the pretreatment reaction and that initially in the yellow grease were about 0.9% and 0.2%, respectively. So, the initial water amount was actually quite small compared to that produced by the reaction. In addition, the total water amount produced in the pretreatment reaction of the 20% palmitic acid mixture was about 1.3% water. The initial water level of 0.2% does not seem to be large enough to explain the difference in the extent of reaction. Yellow grease generally contains some unsaponifiable material and this may also affect the pretreatment reaction. This material is almost certainly the cause of the interphase material that accumulated between the ester and wash water

after the main transesterification. The interphase material will be discussed in a later section.

The reason for the differences between the simulated feedstock and the yellow grease is still under investigation. Even though the recipes for the pretreatment that were developed using the synthetic feedstock needed to be changed, the parametric studies were still considered to be useful since they identified the effects of the variables and made the required changes in the process easy to predict.

Previous experience had shown that to get the FFA below 1 mg KOH/g after the second pretreatment step, the first step needed to get the FFA level to approximately 5 mg KOH/g. Therefore, the first step was repeated with the molar ratio increased to 20:1 and the reaction time increased to 1 h. At this time, the acid value of the oil mixture was measured to be 5.22 mg KOH/g after the first step reaction.

Using the material from the first pretreatment step, the reaction was continued for the second step at three different molar ratios with 5% sulfuric acid for 1 h. The changes in the acid value of the mixture are shown in Table 5. The acid value of the mixture decreased to as low as 0.74 mg KOH/g with a 40:1 molar ratio of methanol to FFA.

To investigate the useful range of the process developed for yellow grease biodiesel production, the pretreatment technique was applied to brown grease with an acid value of 66.08 mg KOH/g, which corresponds to a FFA level of about 33%. The fatty acid composition of the brown grease was not available. Initial tests showed that a two–step pretreatment reaction with 20:1 molar ratio and 5% H₂SO₄ catalyst did not reduce the FFA to less than 2 mg KOH/g. A third step was needed with a 40:1 molar ratio. Three steps of pretreatment were considered to be undesirable because the extra step of pretreatment requires more time, more alcohol, and as will be shown later, reduces the yield. When the sulfuric acid catalyst amount was increased to 10%, the acid values after the first and second steps were reduced to around 5 mg KOH/g and 2 mg KOH/g, respectively. Therefore, the final recipe for the high FFA pretreatment consisted of a 1–h reaction time, 10% sulfuric acid amount, and 20:1 molar ratio for the first step, and a 40:1 molar ratio for the second step. The changes in the

Table 5. Effect of molar ratio on acid value in second step at 5% catalyst amount.

Methanol molar ratio	Reaction time (hours)	Acid value (mg KOH/g)
Before test	–	5.22
20:1	1.0	1.64
30:1	1.0	1.19
40:1	1.0	0.74

Table 6. Effect of 10% catalyst amount on the acid value in 2 steps pretreatment reaction.

Methanol molar ratio	Run 1	Run 2
Before test	66.08	66.08
1st step (20:1)	5.20	5.10
2nd step (40:1)	2.08	1.98

Table 7. Effect of different catalysts on transesterification of yellow grease^[a].

Catalyst	Catalyst amount (g) ^[b]	Catalyst amount as metal base	Total glycerin (%)	Free glycerin (%)	Yield (%)
KOH	3.5 g (1%) 0.30 g (to neutralize)	0.7% K	0.23	0.014	74.8
KOH	1.75 g (0.5%) 0.30 g (to neutralize)	0.35% K	0.23	0.016	74.3
NaOH	2.13 g (0.61%) 0.49 g (to neutralize)	0.35% Na	0.23	0.017	81.2
NaOCH ₃	2.87 g (0.82%) 0.49 g (to neutralize)	0.35% Na	0.20	0.011	80.5
Na	1.22 g (0.35%) 0.49 g (to neutralize)	0.35% Na	0.20	0.013	82.2

^[a] After the pretreatment reactions with 20:1 and 40:1 molar ratios in the 1st and 2nd step reactions, respectively, and 5% sulfuric acid catalyst.

^[b] The catalyst amounts were calculated based on 0.74 mg KOH/g acid value of the 400 g yellow grease, which initially had 12% FFA.

acid value of the mixture are shown in table 6. By increasing the acid catalyst amount, very high levels of FFA could be processed with a 2-step pretreatment.

ALKALINE CATALYZED TRANSESTERIFICATION

To investigate the effect of different alkaline catalysts on the transesterification of yellow grease, potassium hydroxide (KOH), sodium hydroxide (NaOH), sodium methoxide (NaOCH₃), and metallic sodium (Na) were used. The molar ratio of methanol to unreacted grease was 6:1 and the metal portion of the catalyst amount was held constant at 0.35% except for one case with KOH where it was doubled to 0.7%. The catalyst amount was calculated based on the initial amount of fat in the yellow grease. Table 7 shows that all the samples met the total glycerin specification (0.24%) but the metallic sodium gave the best yield. The yield was calculated by dividing the final weight of ester by the initial weight of yellow grease.

A similar investigation was conducted for brown grease. Pretreated brown grease was processed with different amounts of KOH and NaOCH₃ at room temperature for 8 hours. NaOCH₃ has the advantage that it is a strong catalyst and it can be purchased, in bulk, already premixed with methanol. This offers considerable safety and convenience over KOH, which needed to be measured and dispensed manually.

Table 8. The effect of different catalyst and amounts on transesterification of brown grease.

Run No.	Catalyst	Catalyst amount (g) ^[a]	Total glycerin (%)	Free glycerin (%)	Yield (%)
6	KOH	1.01 g (0.5%) 0.61 g (to neutralize)	1.91	–	56.4
7	KOH	0.50 g (0.25%) 0.61 g (to neutralize)	9.22	–	–
8	NaOCH ₃	0.82 g (0.41%) 1.0 g (to neutralize)	0.19	0.004	67.0
9	NaOCH ₃	0.42 g (0.21%) 1.0 g (to neutralize)	0.18	0.002	75.1

^[a] The catalyst amounts were calculated based on 2.03 mg KOH/g acid value of the 300 g brown grease which initially had 33% FFA.

Table 8 shows the results from processing brown grease that had been pretreated with the 2-step process. To investigate the effect of different catalyst amounts, 0.5% and 0.25% KOH and 0.41% and 0.21% NaOCH₃ were used. The actual alkaline catalyst amounts used were calculated as a percentage of the unreacted grease plus a calculated amount needed to neutralize the free fatty acids remaining in the mixture. The methanol molar ratio was 6:1.

When 0.25% KOH was used as an alkaline catalyst in the transesterification, almost no reaction was observed. When the catalyst amount was increased to 0.5%, some reaction occurred but it was not enough to meet the total glycerin specification for biodiesel. When the catalyst was changed to NaOCH₃ at 0.21%, the total glycerin amount and the yield were acceptable at 0.18% and 75.1%, respectively. However, a further increase of the NaOCH₃ gave lower yield and higher total glycerin due to more soap formation.

Mass Balance of the Methyl Esters Produced from Feedstock with High FFA

After the reaction has been completed with the alkaline catalyst, the yield from the different process options can be compared. Table 9 shows the mass balance of oil and ester for brown grease processed with two and three pretreatment steps. When the methanol-water mixture was removed at the end of each pretreatment step, it also carried a significant amount of fat and ester with it. To find the amount of fat and ester lost in the pretreatment, the methanol-water mixture removed after each step was heated on a hot plate. After evaporating the methanol and water, the remaining material was weighed.

Table 9. The losses in pretreatment and transesterification.

Run No.	Catalyst ^[a]		Feedstock (g)	Ester (g)	Yield (%)	Interphase (g)	Ester/fat loss in pretreatment (g)		
	%	Total amount (g)					1st step	2nd step	3rd step
1	0.82 NaOCH ₃	3.53	400	–	–	326.18	38.26	20.63	9.85
2	0.41 NaOCH ₃	1.82	300	151.83	51.91	91.24	26.07	16.87	8.67
3	0.21 NaOCH ₃	1.42	300	164.95	56.39	84.21	26.07	16.87	8.67
4	0.10 NaOCH ₃	1.20	300	161.94	55.36	85.96	24.96	18.09	5.75
5	0.05 NaOCH ₃	1.10	300	162.58	55.58	93.20	24.96	18.09	5.75
6	0.5 KOH	1.61	300	163.57	56.40	100.83	31.94	4.74	–
7	0.25 KOH	1.11	300	47.21	–	218.80	31.94	4.74	–
8	0.41 NaOCH ₃	1.82	300	200.90	66.97	60.40	31.11	5.23	–
9	0.21 NaOCH ₃	1.42	300	225.36	75.12	37.12	31.11	5.23	–

^[a] The catalyst amounts were calculated based on 2.03 mg KOH/g acid value of the brown grease, which initially had 33% FFA.

The fat and ester amounts are shown in Table 9. When the number of steps was reduced from three to two, the yield was increased because less of the fat and ester were removed. In commercial production, this material would probably be returned to the process to maximize the yield. In recognition of the losses when the methanol–water mixture is removed, it was decided that the methanol–water mixture would not be removed after the last step of pretreatment. The small amount of water present in the mixture at this point does not seem to affect the reaction.

The catalyst amount used in transesterification was another factor that affected the yield. When excess alkaline catalyst was used in the transesterification, it increased the soap amount and the interphase. Interphase was the name given to a middle phase that appeared during the washing process between the animal fat ester and the wash water. The composition of the interphase has not been determined but it is insoluble in both the ester and water. Interphase was never observed when processing soybean oil, lard, tallow, or the synthetic high FFA feedstock. It apparently originates from unsaponifiable material in the yellow and brown grease and may be calcium based since it was found only in animal fat greases. After the 4th washing step, the interphase was separated from the ester. During the separation, some ester was unavoidably removed with the interphase. The amount of interphase decreased when the number of pretreatment steps was decreased from three to two.

The Effect of Solubility of Methanol in the Oils and Methyl Ester

To understand the losses of ester and fat in the pretreatment process, the solubility of the reactants with methanol was studied as a function of temperature. Soybean oil, lard, yellow grease methyl ester (YGME), yellow grease, and brown grease were mixed with equal volumes of methanol at 60°C for 1 h. No catalyst was added so chemical reaction was assumed to be negligible. Table 2 shows that some reaction can occur between FFAs and methanol even without catalyst. In addition, the catalyst may affect the solubility of methanol in the yellow grease. For these reasons, the data presented here should not be taken as representative of actual reaction conditions. However, they do explain the processes that occur during the pretreatment process.

After mixing, the mixture was placed in a constant temperature bath. Each hour the temperature was reduced in 10°C decrements starting with 60°C. At each temperature, two samples were drawn from the upper and lower phases of the mixture and the samples were heated on a hot plate to evaporate the methanol. After evaporation, the percentages of methanol in the lower phase and the upper phase were calculated. Figure 3 shows the solubility of the reactants in methanol at the different temperatures. The solubility of methanol in soybean oil and lard was low and about the same for both compounds. This indicates that the solubility is not affected by the saturation of the oil or fat. However, the solubility of the oil was strongly related to its FFA level and ester amount. When the two greases with different FFA levels (9% and 33%) are compared, it can be seen that the methanol solubility increases with higher FFA. The solubility of the methanol in YGME was the highest among the samples. The YGME formed a single phase with methanol at 40°C. These data show why the yield decreased when the higher FFA

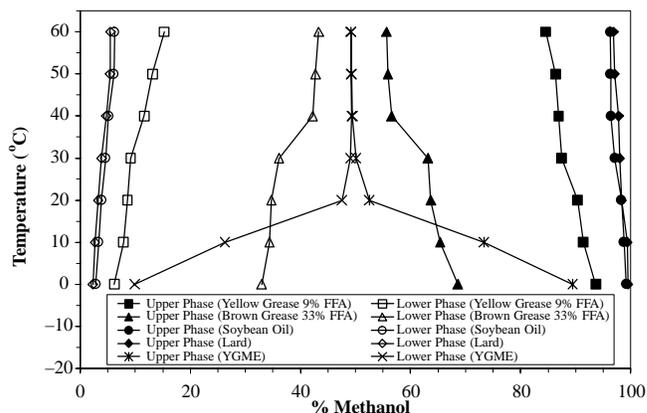


Figure 3. Solubility of soybean oil, lard, YGME, yellow grease, and brown grease in methanol.

feedstocks were processed. At the higher FFA levels, the methanol–water mixture removed during pretreatment was carrying a greater amount of methyl ester and unreacted fat. This problem can be addressed by separating the methanol and water from the material removed during pretreatment and returning the residue to the process stream.

CONCLUSIONS

The objective of this study was to investigate the use of low-cost, high FFA feedstocks to produce fuel-quality biodiesel. It was determined that feedstocks with high FFAs could not be transesterified with the traditional alkaline catalysts that have been used with good success for vegetable oils. Alkaline catalysts form soap when they react with the FFAs. Soap removes the catalyst from the reaction and prevents the separation of the glycerin and the ester.

A process was developed to use acid catalysts to pretreat the high FFA feedstocks until their FFA level was below 1%, allowing the subsequent use of alkaline catalysts to convert the triglycerides. The effects of the methanol molar ratio, acid catalyst amount, and reaction time on the reduction of FFA level were studied with a simulated high FFA feedstock consisting of 20% palmitic acid in soybean oil. This part of the study showed that the FFA level of the feedstocks could be reduced to less than 1% with a 2-step process of acid-catalyzed pretreatment. Extension of the process to yellow and brown grease showed that higher levels of acid catalyst and methanol were required.

The following specific conclusions are based on the process development portion of this project.

1. The acid-catalyzed pretreatment reaction decreased the acid value of the synthetic mixture to less than 2 mg KOH/g with a 2-step process. Using the 2-step acid catalyzed pretreatment followed by an alkali-catalyzed final reaction, the transesterification reaction was completed in much less time than would be possible with acid-catalyzed transesterification alone.
2. Increasing the acid catalyst amount is very effective in decreasing the acid value of the mixture. In the first pretreatment step, using a 10:1 molar ratio and 30 min of reaction time, the acid value of the simulated high FFA feedstock was reduced from 41.33 mg KOH/g to 1.37 mg KOH/g using 15% acid catalyst.
3. Ethanol decreased the FFA level of the synthetic mixture faster than methanol.

4. With KOH as the alkaline catalyst, it was found that the acid value of the feedstock needed to be reduced to 1 mg KOH/g (0.5% FFA) in order to get good ester conversion.
5. The two-step acid catalysis pretreatment process was successful in decreasing the acid value of yellow and brown grease to less than 2 mg KOH/g but a higher molar ratio and more time were required than was expected based on the work with the simulated high FFA feedstock.
6. It was observed that the alkaline catalyst amount and type affect the transesterification reaction completeness and yield. NaOCH₃ is more effective than KOH. The best result for the high free fatty acid feedstock was obtained with 0.21% NaOCH₃ following a 2-step pretreatment. The yield and total glycerin were 75.12% and 0.18%, respectively.

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