A PILOT PLANT TO PRODUCE BIODIESEL FROM HIGH FREE FATTY ACID FEEDSTOCKS

M. Canakci, J. Van Gerpen

ABSTRACT. *Biodiesel is an alternative diesel fuel consisting of the alkyl monoesters of fatty acids from vegetable oils or animal fats. Currently, most biodiesel is made from soybean oil, methanol, and an alkaline catalyst. However, there are large amounts of fats and oils that are unsuitable for human consumption that could be converted to biodiesel at lower cost. The problem with processing these waste oils is that they often contain large amounts of free fatty acids that cannot be converted to biodiesel using an alkaline catalyst. These free fatty acids react with the alkaline catalyst to produce soaps that inhibit the separation of the biodiesel, glycerin, and wash water. Previous research has developed a process for pretreating these high free fatty acid feedstocks using acid catalysts, which do not form soaps. The objective of this study was to construct a pilot plant to produce biodiesel from a wide variety of feedstocks including those with high free fatty acids. A 190 L batch pilot plant has been built that can process high free fatty acid feedstocks using an acid–catalyzed pretreatment followed by an alkaline–catalyzed transesterification. Case studies of pilot plant–scale production of biodiesel from soybean oil, yellow grease with 9% free fatty acids, and brown grease with 40% free fatty acids are presented. The effect of varying the reaction parameters is discussed, and the separation and washing processes are described. Estimates of the fuel cost using different feedstocks are also provided.*

Keywords. *Alternative fuel, Biodiesel, Diesel, Fuel, Methyl ester.*

Research into methyl esters as an alternative diesel fuel has been going on for more than 20 years. This work has intensified in the past 5 to 6 years as biodiesel's emissions benefits have become more widely understood (Chang and Van Gerpen, 1997; Schumacher and Van Gerpen, 1996; Schmidt and Van Gerpen, 1996; Zhang and Van Gerpen, 1996; Chang et al., 1996; Sharp, 1998; Graboski and McCormick, 1998). Virtually all previous work was based on the methyl esters of fatty acids from soybean oil. Soybean oil was chosen because, in the U.S., soybean oil is the only oil that is available in sufficient quantity to supply a national market. However, the high cost of food–grade soybean oil limits its use in diesel engines. Reducing the cost of the feedstock is necessary for biodiesel's long–term commercial viability. One way to reduce the cost of this fuel is to use less expensive feedstocks like waste restaurant oils and rendered animal fats. Currently, rendered animal fats and restaurant greases are sold commercially as animal feed. If the free fatty acid (FFA) level is less than 15%, it is called "yellow grease." During the summer months, the FFA levels of the animal fats may exceed 30%. This seasonal variation is caused by the accelerated decay of animal carcasses at high ambient temperatures. These lower quality fats may be blended with low FFA fats and sold as yellow grease or sold directly at a discounted price as "brown grease." An earlier article described the development of a robust chemical process for converting these high–FFA feedstocks to biodiesel (Canakci and Van Gerpen, 2001). The objective of the current study was to develop a pilot plant to implement this process and to provide a facility for further research, demonstration, and training.

Restaurant waste oils and rendered animal fats are less expensive than food–grade soybean oil. Approximately 1.1 billion kg of waste fats are collected annually from restaurants and fast–food establishments in the U.S. (Haumann, 1990). These waste oils usually contain significant amounts of free fatty acids that cannot be converted to biodiesel using an alkaline catalyst due to the formation of soaps. The soaps can prevent separation of the biodiesel from the glycerin during processing. An alternative process is to utilize acid catalysts that do not form soaps (Aksoy et al., 1988; Freedman and Pryde, 1982; Liu, 1994). Previous work has demonstrated that acid catalysts are too slow to be practical for converting triglycerides to biodiesel (Canakci and Van Gerpen, 1999). However, acid catalysts appear to effectively convert FFAs to esters. Previous work has developed an acid–catalyzed pretreatment process to convert the FFAs to esters followed by alkaline–catalyzed transesterification of the triglycerides (Canakci, 2001; Canakci and Van Gerpen, 2001). A disadvantage of the acid–catalyzed processes is that the reaction of FFAs with alcohol produces water, which inhibits the esterification of the FFAs and the transesterification of the glycerides (Romano, 1982; Freedman et al., 1984; Feuge et al., 1945; Canakci and Van Gerpen, 1999).

Article was submitted for review in September 2001; approved for publication by the Power & Machinery Division of ASAE in February 2003. Presented at the 2001 ASAE Annual Meeting as Paper No. 016049.

The authors are **Mustafa Canakci,** Assistant Professor, Kocaili University, Izmit, Turkey; and **Jon H. Van Gerpen, ASAE Member Engineer,** Professor, Department of Mechanical Engineering, Iowa State University, Ames, Iowa. **Corresponding author:** Jon H. Van Gerpen, Department of Mechanical Engineering, Iowa State University, Ames, IA 50011; phone: 515–294–5563; fax: 515–294–3261; e–mail: jvg@iastate.edu.

Vol. 46(4): 945–954

Hawkins and Fuls (1982), Hassett and Hasan (1982), Nye and Southwell (1983), Fuls et al. (1984), Peterson et al. (1991), Mittelbach and Tritthart (1988), and Peterson et al. (1995) have all described production of biodiesel in pilot–plant quantities. These published results were investigated to determine whether any unique processes were required to scale–up from laboratory scale to pilot plant scale. While there is considerable variation in the processes used, none of these studies identified any special problems associated with the scale–up.

PILOT PLANT PROCESS AND EQUIPMENT

An extensive study to develop a robust process for converting high–FFA feedstocks to biodiesel was described in a previous publication (Canakci and Van Gerpen, 2001). This study showed that an acid–catalyzed pretreatment could be used to reduce the FFA level of the feedstocks to below 1%. These feedstocks could then be converted to biodiesel using an alkaline–catalyzed process. A novel feature of this process was that the acid–catalyzed pretreatment was conducted in two or more steps with a separation process between the steps to remove the water formed during the reaction, which inhibits the completion of the reaction. After finding the best strategy for the small–scale transesterification of feedstocks with high FFAs, a pilot plant was designed to implement the strategy. The strategy was described in Canakci and Van Gerpen (2001). The pilot plant was assembled at the Iowa Energy Center's Biomass Energy Conversion Center (BECON) in Nevada, Iowa.

The pilot plant consists of two units: a pretreatment unit to reduce the FFA level of the yellow grease to less than 1%, and a main reaction unit for transesterification. When a low–FFA feedstock such as soybean oil is used, only the main reaction unit is needed. When a high–FFA feedstock is used, it must pass through the pretreatment unit before entering the main reaction unit. The design of the pilot plant is described below.

PRETREATMENT UNIT

A schematic of the pretreatment unit is shown in figure 1. Feedstocks with high FFAs (yellow grease or brown grease) are delivered to the BECON facility by truck and stored in a 1900 L heated, agitated, cone–bottom storage tank. The tank of animal fat feedstock is kept at 55°C to 60°C using a 1200 W heater to prevent solidification. Agitation is provided by a 0.25 kW recirculating pump. A 20–micron cellulose filter is used to remove insoluble materials, such as meat and bone particles, from the yellow or brown grease. A pump, identified on the schematic as P 2p, transfers the feedstock to the 34 L stainless steel pretreatment reaction tank. A load cell is used to measure the weight of feedstock transferred to the reaction tank. The alcohol solution with acid catalyst is prepared and added to the reaction tank using the air–operated pump (P 1). The methanol is supplied directly from 208 L drums. Recirculation by a 0.37 kW pump (P 3p) provides agitation for the process, and the temperature of the mixture during pretreatment is maintained at 60°C by a 3000 W heater installed in the recirculation loop.

When the FFAs react with alcohol to form esters, water is formed in the products. It is necessary to separate the water from the pretreated material since it will inhibit further reaction.

When the first step of the pretreatment has reached steady state after 1 h, the reactants are transferred to a 454 L stainless steel settling tank. This tank is used to separate the methanol–water mixture from the feedstock. After a resi–

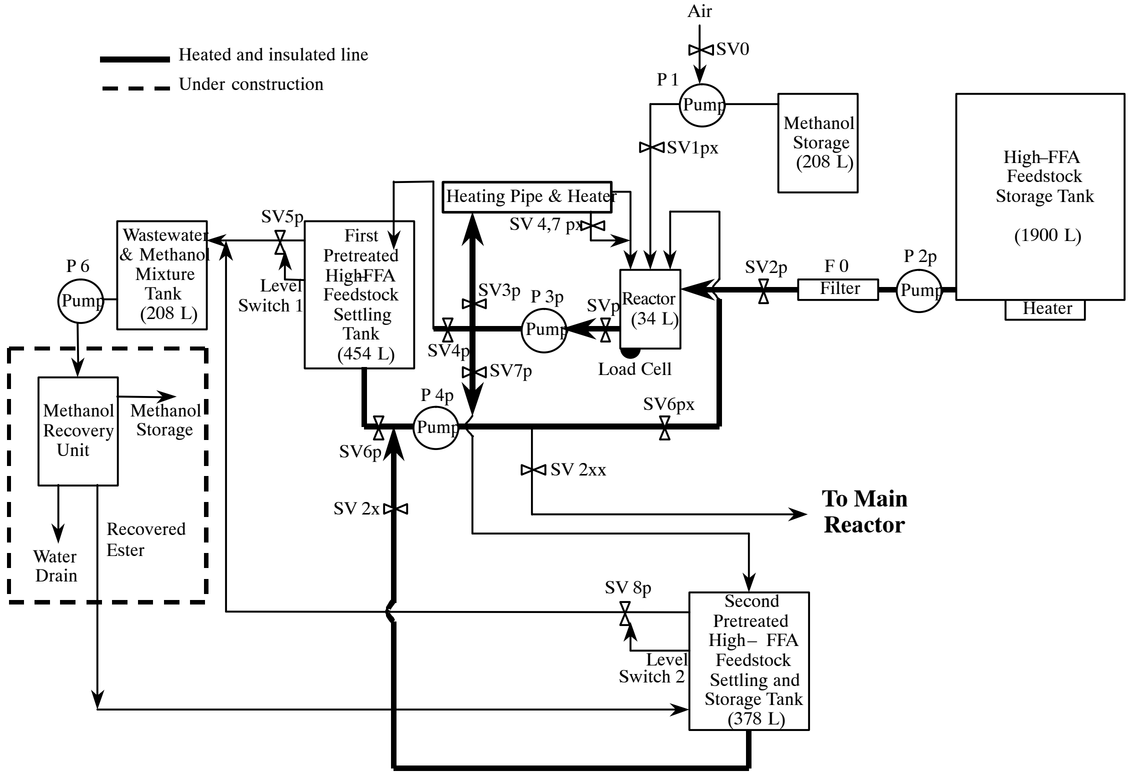


Figure 1. Flow diagram of the pretreatment unit of the pilot plant.

dence time of approximately 24 h, the methanol and water rise to the top of the tank where they can be removed as a single phase. Level switches mounted in the tanks control solenoid valves, which drain the methanol–water mixture to a 208 L waste tank. Although not currently installed in the pilot plant, future plans call for this methanol–water mixture to be processed and the methanol recovered.

For the second step of pretreatment, a pump (P 4p) transfers the feedstock from the first pretreatment settling tank back to the pretreatment reaction tank, and additional methanol–acid mixture is added. Pump P 3p recirculates the mixture for 1 h at 60°C and then pumps the mixture to a 378 L stainless steel tank for a second settling process. At this point, the free fatty acid level of the feedstock has been reduced to less than 1%. Pretreated feedstock is then transferred from the second pretreatment settling tank to the main reaction tank using pump P 4p.

TRANSESTERIFICATION (MAIN) UNIT

A schematic of the main reaction unit is shown in figure 2. Soybean oil is stored in a 1900 L cone–bottom tank at room temperature. If soybean oil is used for the transesterification reaction, the 1900 L tank's 0.25 kW pump (P 2) transfers the soybean oil to the main reaction tank. If pretreated high–FFA feedstock will be used for the transesterification, then pump P 4p is operated to bring the pretreated material in from the second–stage settling tank. The main transesterification reaction takes place in a 265 L, stainless steel reaction tank with a 0.37 kW explosion–proof mixer, which has a fixed speed of 1750 rpm. A load cell mounted on one leg of the reaction tank measures the reactant amounts. To ensure accurate weight measurements, all connections to the tank are flexible, and the load cell output has been calibrated by adding known amounts of water to the tank.

Methanol is added to the reaction tank using air–operated pump P 1. After preparing the alcohol solution with the catalyst, it is added to the reaction tank. The reactants are agitated for 8 h, and then the mixture is transferred to a 492 L cone–bottom tank for glycerin separation and ester washing. A load cell measures the glycerin amount, the washing water amount, and the amount of ester produced. A Micro Motion coriolis–type density meter installed at the exit of the separation tank identifies the glycerin, water, and ester interfaces during the separation processes. Pump P 4 transfers the glycerin to the glycerin storage container. Presently, no glycerin clean–up equipment is included in the pilot plant, and glycerin is disposed of as a waste product. Future plans include recovery of the methanol that is removed with the glycerin.

Upon glycerin removal, the ester is washed to remove residual catalyst and soap. The hardness of the city water of Nevada, Iowa, has been measured to be 7.2 grains/L by MVTL Laboratories, Inc., Nevada, Iowa. For better washing, a water softener and a 190 L water heater were used to prepare the wash water. Four sprinklers were mounted on the top of the tank so that the wash water droplets are distributed uniformly over the surface of the ester. The wash water temperature was set to be 60°C. Tests showed that warm water was much more effective at removing soap and free glycerin from the ester than cold water. Pump P 4 is used to recirculate the washing water, to transfer the water to the waste outlet, and to move the finished ester to the storage tanks. Separate storage tanks are used for biodiesel from high–FFA feedstocks and for biodiesel from vegetable oil. Pump P 5 is used to transfer the biodiesel to external storage

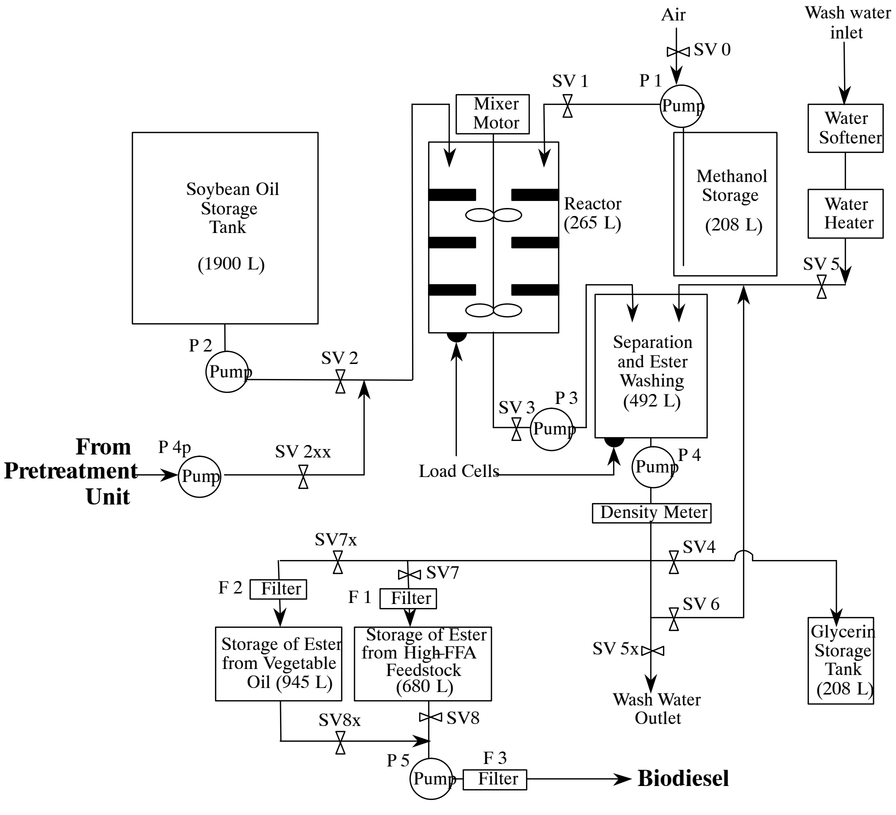


Figure 2. Flow diagram of the transesterification (main) unit of the pilot plant.

tanks and barrels. The esters are filtered with 20–micron cellulose filters when pumped to the external storage tanks. At the present time, the fuel is not dried because it is used within a short time. The residual dissolved water in the fuel can contribute to hydrolysis of the fuel to free fatty acids over time. A flash–type drying system has been designed and will be added in the future.

PILOT PLANT OPERATION AND ANALYSIS

The pilot plant described in the previous section was used for preparation of methyl esters from soybean oil, yellow grease, and finally brown grease. The following sections describe the adaptation of the small–scale processes to pilot plant–scale biodiesel production. This adaptation process is presented using three specific case studies.

Case Study 1: Biodiesel Production from Soybean Oil

The first case study describes biodiesel production from soybean oil. This case study also demonstrates how a two–step reaction can provide very low total glycerin levels. The process was started by dissolving the potassium hydroxide (KOH) catalyst in methanol at room temperature in the main reaction tank. The ingredient amounts for the batch described above were: 181.2 kg soybean oil, 39.4 kg methanol (6:1 molar ratio), and 1.8 kg KOH (1% of oil by weight). The soybean oil was then added to the reaction tank at room temperature, and the mixture was agitated for 8 h. Samples of the mixture were extracted at 1 h intervals, and the total glycerin level of the ester fraction was measured using AOCS Official Method Ca 14–56, known as the total, free, and combined glycerol (iodometric–periodic acid) method (AOCS, 1991). These data are shown in table 1. As can be seen, the reaction was essentially complete after 4 h. However, the total glycerin amount was also too high at the end of the reaction. Fuel–quality biodiesel needs to have a total glycerin level that is less than 0.24%. Additional testing showed that the level of agitation in the tank was insufficient. Stationary vanes were added to the main reactor to prevent the fluid from rotating as a solid body. After this change, the total glycerin level was below the required level.

Although the reaction was now capable of producing fuel with a low glycerin level, the data for several batches with insufficient agitation are included here to demonstrate how a second transesterification step can be used to recover biodiesel with excessive total glycerin level and to provide a final product with an extremely low total glycerin level.

When it was found that the biodiesel produced did not meet the total and free glycerin specifications, the biodiesel was reacted again with fresh methanol–KOH solution. This time, the methanol amount used was a 3:1 molar ratio based on the initial amount of oil, and the KOH was 0.1% of the initial weight of oil. As shown in table 2 for the tests designated as run 1 and run 2, after the second step of transesterification, the total glycerin level of the biodiesel easily met the 0.24% specification. The yield shown in the table is the weight of ester produced divided by the original weight of oil.

The third run shown in table 2 was different from the others. The oil used was a refined, bleached, and deodorized (RBD) oil, while the oil used for other runs was a water–degummed oil with some residual phospholipids. As shown in the table, the third run has a higher yield than the first two. Freedman et al. (1984) has stated that the phosphorus in the oil leads to catalyst destruction and reduces the ester yield.

In run 4, a different method was used for the two–part transesterification reaction. The total amount of methanol–KOH solution was based on a 6:1 molar ratio for methanol, and the KOH was 1% of the weight of the oil. One fourth of the methanol solution was held back to use later. The vegetable oil at room temperature was then added. The reactants were mixed for 4 h at atmospheric pressure and room temperature. After 4 h, the mixture was settled for 30 min, and the glycerin that collected at the bottom of the reactor was pumped to the separation tank. The methanol solution that had been held back was then added, and the reaction was continued for another 3 h. This procedure gave very low levels of total glycerin, as shown in table 2. This showed that fuel–quality biodiesel could be produced using the same quantity of methanol and catalyst and the same amount of time as had been expected from the small–scale testing. These tests demonstrated that even with inadequate agitation, extremely low levels of total glycerin could be obtained with a two–step process.

Case Study 2: Biodiesel Production from Yellow Grease

This section describes a case study of the use of the pilot plant to produce biodiesel from yellow grease. The yellow grease was supplied by National Byproducts, a rendering company located in Des Moines, Iowa. The fatty acid distribution of the yellow grease is shown in table 3.

The first step in the processing of yellow grease was to filter out the insoluble materials, such as meat and bone particles, at around 55°C to 60°C. Then, the two–step acid–catalyzed reaction described earlier (Canakci and Van Gerpen, 2001) was applied to the feedstock to reduce its FFA level to less than 1%. The specific fat used for this case study had an acid value of 18.03 mg KOH/g, which corresponds to an FFA level of about 9%. The acid values were measured

Table 1. Total glycerin change during the transesterification of soybean oil.

Time (h)	Total Glycerin (%)
0	11.07
1	1.09
2	0.79
3	0.69
4	0.62
5	0.56
6	0.54
7	0.53
8	0.52

Table 2. Measured values of the biodiesel prepared from soybean oil.

Run	Reaction	Total Glycerol (%)	Free Glycerin (%)	Yield (%)
1	After 1st	0.50	—	—
	After 2nd	0.02	0.014	94.6
2	After 1st	0.48	—	—
	After 2nd	0.03	0.021	94.7
3	After 1st	0.52	—	—
	After 2nd	0.06	0.021	97.2
4	Two–step	0.07	0.002	94.8

Table 3. Fatty acid composition of the soybean oil, yellow grease, and brown grease, and their methyl esters produced in the pilot plant.

	Carbon Chain (%)[a]											
Product	C14:0	C15:0	C16:0	C16:1	C17:0	C18:0	C18:1	C18:2	C18:3	C20:0	Unknown Components	Sat. (%)
Soybean oil	—	—	10.58	—	0.11	4.76	22.52	52.34	8.19	0.36	0.48	16.29
Soybean oil methyl ester	—	—	10.56	—	0.11	4.74	22.51	52.39	8.22	0.36	0.44	16.26
Yellow grease	2.43	0.37	23.24	3.79	1.00	12.96	44.32	6.97	0.67	0.14	1.11	39.76
Yellow grease methyl ester	2.42	0.36	22.77	3.84	0.95	12.03	44.98	7.80	0.79	0.14	1.24	38.67
Brown grease	1.66	0.18	22.83	3.13	0.55	12.54	42.36	12.09	0.82	0.20	0.80	38.16
Brown grease methyl ester	1.63	0.19	22.84	3.06	0.58	12.94	42.51	11.61	0.79	0.21	0.73	38.39

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

Table 4. Ingredient amounts used in the pretreatment reaction of yellow grease with 9% FFA for one batch.

Reactant	First Step	Second Step
Feedstock	20 kg	20 kg
Methanol	4.35 kg	2.13 kg
Sulfuric acid	0.087 kg	0.021 kg

Table 5. Ingredient amounts for transesterification of pretreated yellow grease for one batch.

Reactant	Amount (kg)
Pretreated yellow grease	176
Methanol	32.6
$NaOCH_3$ (0.82%)	1.22
$NaOCH_3$ (to neutralize)	0.28

using AOCS Official Method Cd 3a–63 for acid value (AOCS, 1998).

After pumping the required amount of filtered yellow grease at 60°C into the pretreatment reaction tank, the methanol solution with sulfuric acid was added to the reaction tank. The pretreatment unit in the pilot plant has a 20 kg capacity for each batch. The ingredient amounts at each stage for one batch are listed in table 4. The first pretreatment consisted of 5% sulfuric acid and a 20:1 molar ratio of methanol, both based on the measured FFA amount. The mixture was recirculated for 1 h through the heating pipe, which kept the mixture temperature between 55°C and 60°C. After 1 h, the mixture was transferred to the first–stage settling tank to separate the alcohol–water mixture from the pretreated yellow grease. At the end of the first stage, the average acid value of the feedstock was measured to be 4.26 mg KOH/g.

For the second stage of pretreatment, the lower phase from the first–stage settling tank was taken back to the pretreatment reaction tank and additional methanol and sulfuric acid solution were added. In this pretreatment stage, the sulfuric acid amount was 5%, and the molar ratio was 40:1, based on the FFA level. Again, the mixture was recirculated for 1 h through the heating pipe to keep the temperature between 55°C and 60°C, and then the mixture was taken to the second–stage settling tank. Originally, the intent was for the water–alcohol mixture to be separated in the second–stage settling tank. However, the water formation in this stage is low (less than 0.1%) and was not expected to significantly affect the alkaline–catalyzed transesterification reactions. Therefore, the alcohol–water mixture was not removed before the main transesterification process.

After pretreatment, the process was continued with the alkaline catalyst (0.82% $NaOCH_3$) at a 6:1 molar ratio of methanol, based on the amount of unreacted triglycerides. The FFA level of the pretreated yellow grease was measured to be 0.85 mg KOH/g, and an additional catalyst amount was added to neutralize these FFAs. While no explicit attempt was made to add additional alkaline catalyst to neutralize the H_2SO_4 left from the second stage of pretreatment, later calculations showed that the amount required to do this was less than 25% of the catalyst that was added. Sodium methoxide catalyst was used because tests had shown that it was a very effective catalyst and it could be purchased already blended with methanol, which made it easier to dispense. The molar ratio of alcohol and the catalyst amount were calculated for the transesterification based on the initial fat amount in the yellow grease. The transesterification process occurred at room temperature for 8 h. The ingredient amounts for transesterification of the pretreated yellow grease for one batch are listed in table 5.

After the reaction, the mixture was pumped to the separation tank, and the ester and glycerin layers were allowed to separate in the tank overnight. However, separation of the glycerin did not occur until water was added. The mixture was washed four times for 30 min with softened warm water to remove the glycerin, excess alcohol, and catalyst. For each washing step, the amount of water was 50% by volume of the ester. During the washing process, a separate phase was noted consisting of material that was not soluble in either the ester or the wash water. This material will be referred to as "interphase." After the fourth washing step, the interphase material that accumulated between the ester and wash water was separated from the ester. Two additional washing steps (for a total of six) were found to be necessary to ensure that the free glycerin level of the ester was within the specification for fuel–quality biodiesel (0.02%). After extracting the wash water–glycerin mixture, the ester was pumped to the storage tank. The total glycerin, free glycerin, and the yield of the ester produced from yellow grease are listed in table 6.

Case Study 3: Biodiesel Production from Brown Grease

The third case study involved pilot plant–scale biodiesel production from brown grease. The brown grease was obtained from the Simonsen rendering plant in Quimby, Iowa, and had an acid value of 79.2 mg KOH/g, which corresponds to an FFA level of almost 39.6%. The fatty acid distribution of the brown grease is shown in table 3.

Table 6. The effect of mixing on the transesterification of pretreated yellow grease.

Feedstock	Total Glycerin (%)	Free Glycerin (%)	Yield (%)
Yellow grease	0.23	0.019	90.2

Table 7. Ingredient amounts used in the pretreatment reaction of brown grease with 39.6% FFA for one batch.

Reactant	First Step	Second Step
Feedstock	15 kg	25 kg
Methanol	14.8 kg	4.3 kg
Sulfuric acid	0.59 kg	0.09 kg

The two–step acid–catalyzed reaction was applied to the feedstock to reduce its FFA level to less than 1%. For the pretreatment reaction of the brown grease with 39.6% FFA, the ingredient amounts are listed in table 7.

The first pretreatment consisted of 10%, by weight, sulfuric acid and a 20:1 molar ratio of methanol based on the amount of FFA in the reactants. The mixture was recirculated for 1 h through the heating pipe at between 55°C and 60°C. When the reaction was complete, the mixture was pumped to the first–stage settling tank to separate the alcohol–water mixture from the pretreated brown grease. The alcohol–water mixture was removed since the water would inhibit the following reaction steps. At the end of the first stage, the average acid value of the feedstock was measured to be 6.96 mg KOH/g (about 3.5 wt%).

In the second stage of the pretreatment, the feedstock from the first–stage settling tank was taken back to the pretreatment reaction tank, and additional methanol and sulfuric acid solution were added in the amounts shown in table 7. In this pretreatment stage, the sulfuric acid amount was 10%, and the molar ratio was 40:1 based on the FFA level of 6.96 mg KOH/g. Again, the mixture was recirculated for 1 h at between 55°C and 60°C. After the reaction, the mixture was taken to the second–stage settling tank, but the alcohol–water mixture was not removed. The water formation in this stage was so low (less than 0.1%) that it would not affect the transesterification reactions. At the end of the second stage, the average acid value of the feedstock was measured to be 1.54 mg KOH/g.

After pretreatment, the process was continued with the alkaline catalyst at a 6:1 molar ratio of methanol. Testing had shown that 0.21% $NaOCH_3$ plus an amount needed to neutralize the free fatty acids was sufficient to complete the reaction. The molar ratio of alcohol and the catalyst amount were calculated based on the initial amount of triglycerides in the brown grease. The ingredient amounts for the main transesterification of the pretreated brown grease are listed in table 8 for one batch.

The transesterification process was conducted at room temperature for 8 h, and then the mixture was pumped to the separation tank. As was the case with the yellow grease, the glycerin phase did not separate. When soft water at 60°C was added to this mixture, a separation did occur, with the ester phase rising to the top and the water–glycerin phase settling to the bottom. These phases were separated by the third phase, which was referred to earlier as interphase material. The mixture was washed six times for 30 min each with soft hot water (60°C) to remove the glycerin, excess alcohol, and catalyst. For each washing, the amount of water was 50% by volume of the ester. After the fourth washing step, the interphase material that had accumulated between the ester and wash water was separated from the ester. After extracting the wash water–glycerin mixture, the ester was pumped to the storage tank. The reaction completion data for the brown grease methyl ester after reaction with the alkaline catalyst are listed in table 9 for two separate runs with different amounts of catalyst.

Table 8. Ingredient amounts for transesterification of pretreated brown grease for one batch.

Reactant	Amount (kg)
Pretreated brown grease	180
Methanol	23.6
$NaOCH_3$ (0.21%)	0.23
$NaOCH_3$ (to neutralize)	0.45

Table 9. Transesterification reaction of the brown grease with 39.6% FFA.

	Amount of $NaOCH_3$ for 180 kg Feedstock						
Run	%	For reaction (kg)	For neutralization (kg)	Total Glycerin (%)	Free Glycerin (%)	Specific Gravity	Yield (%)
1	0.41	0.45	0.45	0.20	0.010	0.8747	63.8
2	0.21	0.23	0.45	0.20	0.018	0.8749	73.9

The results show that the total glycerin level is within the fuel specification (0.24%). They also show that when the higher level of catalyst was used, the soap formation was increased and the ester yield was reduced. The glycerin separation problem was found for both concentrations of sodium methoxide that were used.

Soap and Catalyst Analysis in Pilot Plant Methyl Ester Production.

To investigate the effectiveness of the washing process in the pilot plant, samples of ester, wash water, and glycerin were collected, and the soap and catalyst amount were measured. The amount of catalyst was measured by titrating the ester, glycerin, and wash water with 0.01N HCl using phenolphthalein indicator, and the soap was determined by continuing the HCl titration to the yellow end point of bromophenol blue (Van Gerpen et al., 1997). Table 10 shows the catalyst and soap levels for the methyl esters produced from soybean oil, yellow grease, and brown grease as described in the three case studies. Note that no data are shown for the glycerin collected from the yellow and brown grease. This is because the glycerin did not separate until the first batch of wash water was added. Table 11 shows the catalyst metal mass balance. This mass balance was con–

Table 10. Analysis of the catalyst amount and soap produced in the pilot plant transesterification reaction.

	Soybean Oil[a]		Yellow Grease[b]		Brown Grease[b]	
Sample	% Cat.	% Soap	% Cat.	% Soap	% Cat.	% Soap
Ester	0	0.015	0	0.012	0	0.014
Wash water						
1	0	0.201	0.110	3.368	0.075	2.677
2	0	0.108	0.073	1.505	0.034	1.032
3	0	0.053	0	0.344	0	0.274
4	0	0.038	0	0.242	0	0.222
5	0	0.029	0	0.241	0	0.221
6	0	0.029	0	0.242	0	0.221
Glycerin	4.774	7.625	—	—	—	—

[a] KOH was used as an alkaline catalyst.

[b] $NaOCH_3$ was used as an alkaline catalyst.

Table 11. Mass balance of the catalyst used in the pilot plant transesterification reaction.

	Soybean Oil	Yellow Grease	Brown Grease
Total input of catalyst	1640 g KOH	915 g $NaOCH_3$	680 g $NaOCH_3$
Total input of pure metal catalyst	1143 g K	389 g Na	289 g Na
Methyl ester	3 g K	1 g	1 g
Glycerin	1076 g K	—	—
Wash water	57 g K	387 g	290 g
Total output of pure metal catalyst	1136 g K	388 g Na	291 g Na

ducted to ensure the accuracy of the soap and catalyst measurements.

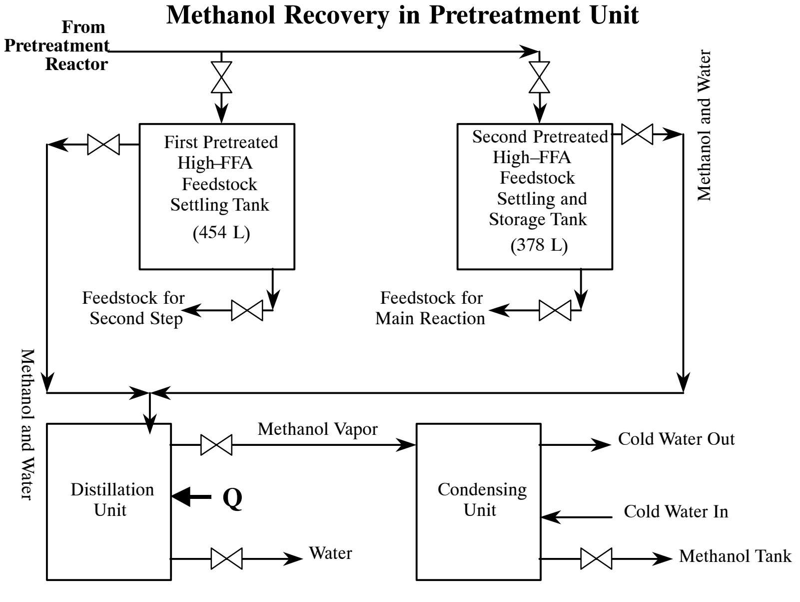
As seen in the tables, most of the catalyst was removed with the glycerin in the transesterification of the soybean oil. For the transesterification of the yellow and brown grease, most of the catalyst was removed with the first two batches of wash water due to the lack of glycerin separation. No catalyst was found in the wash water after the second washing, but soap was still found in the following washing steps. The total amounts of potassium (K) and sodium (Na) output were very close to the input amounts. This confirms the accuracy of the measurements and that most of the catalyst and soap were removed from the biodiesel. Table 10 indicates that some soap was still being removed from the ester on the sixth washing step. However, the sodium balance from table 11 shows that very little soap remains. In addition, although the interphase was not analyzed, the sodium balance indicates that it cannot contain much sodium. Therefore, it is probably not a sodium soap compound. Investigation is continuing, but this material is suspected to be calcium–based or protein–based since it was only found in the rendered animal fats.

Table 12. Market prices of the feedstocks and chemicals used in the calculation.

Feedstock/Chemical	Minimum	Baseline	Maximum
Soybean oil ($/kg)	0.33	0.44	0.55
Yellow grease ($/kg)	0.18	0.29	0.40
Brown grease ($/kg)	0.11	0.20	0.29
Methanol ($/L)	0.092	0.106	0.119
Sulfuric acid ($/kg)	0.045	0.051	0.056
Sodium methoxide ($/kg)	1.32	1.43	1.54

ECONOMIC ANALYSIS OF BIODIESEL PRODUCTION

An economic analysis of the methyl esters produced in the pilot plant was conducted based on a 190 L batch of biodiesel. The plant operating costs for producing biodiesel from feedstocks with high FFAs and from soybean oil were computed. The capital, plant construction, and labor costs were not included. However, the capital cost for a plant that processes yellow and brown grease will be somewhat higher than for soybean oil because of the need for pretreatment equipment. Twelve–month average prices of the feedstocks and chemicals were taken as a baseline case (1999–2000). To investigate the sensitivity of the operating cost to variations in the feedstock costs, a minimum and maximum price were estimated from the annual market average price variations over the last five years (Rudbeck, 2000; USDA, 2000;


Methanol Recovery in Pretreatment Unit

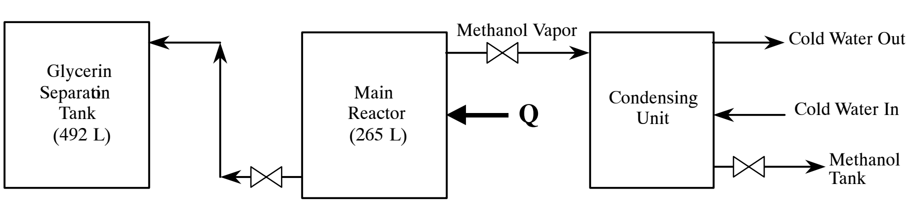

Methanol Recovery in Main Unit

Figure 3. Methanol recovery diagrams.

Table 13. Utility costs for biodiesel production.

Type of Cost	Cost Amount
Natural gas	\$ 0.118 / m^3
Electricity	\$ 0.062 / kW–h
Water	\$ 0.49 / m^3

Chemical Industry Online, 2000). These price assumptions are shown in table 12.

In the cost analysis, glycerin recovery has not been included because the clean–up costs are still uncertain. The value of the glycerin could partially offset the capital costs, which have not been included. However, it was assumed that the excess methanol used in the pretreatment and transesterification reactions was recovered. The methanol recovery system used for the calculations is shown in figure 3. The methanol–water mixture that is removed from both the first– and second–stage settling tanks is directed to a distillation unit, where the methanol is vaporized and then condensed before being returned to the methanol storage tank. Although this equipment is not currently installed on the pilot plant, it is included as a part of future expansion.

A second methanol recovery system was assumed to be used after the main transesterification unit. Since the methanol from the pretreatment unit contains some water, it requires a separate distillation unit to separate the methanol from the water. Therefore, the main reaction recovery unit was separated from the pretreatment recovery unit. Other operating costs, such as the natural gas price for the methanol recovery, electricity, and water costs were included to determine the final biodiesel price. Table 13 lists these utility prices, which are based on current (October 2000) data in Ames, Iowa.

The pump used in the first step of pretreatment to transfer the feedstock and for 1 h of recirculation has a 0.373 kW maximum power requirement, and the heater consumes 3 kW of power. The pump was assumed to be used for 1.5 h for each 20 kg of feedstock, including the transfer of the feedstock into and out of the pretreatment reactor. The same process was repeated nine times to reach the 180 kg capacity of the main reactor. The heater was assumed to be used for 20 min to reach 60˚C during recirculation of the reactants. In the methanol recovery calculation, the heat of evaporation for methanol was taken as 1,185 kJ/kg. The heat required to raise the other compounds from 60˚C to the boiling temperature of methanol (65˚C) was not included as this was expected to be small and could be partially supplied by heat recovery from the condensing methanol. The lower heating value for the natural gas was assumed to be 49,216 kJ/kg, and the fuel was assumed to be burned with 80% of its heating value supplied to the fluid. The methanol amount calculated for the recovery was assumed to be the excess methanol beyond the stoichiometric amount. The mixer used in the transesterification for 8 h consumed 0.373 kW of power. The pumping time for the feedstock into and out of the main reactor was assumed to be 2 h, and the pump was used for another 2 h in the washing process. Thus, the 0.373 kW pump was on for a total of 12 h during the reaction, giving a total of 4.78 kW–h of electrical power consumed.

Comparison of the Costs of the Methyl Esters Produced in the Pilot Plant

A sample calculation for 180 kg of yellow grease with 9% FFA (case study 2) is shown in table 14 for the baseline price case. As mentioned earlier, the pretreatment reactor on the pilot plant has a 20 kg capacity, so it is necessary to run nine batches through this reactor to pretreat a single batch for the main reactor. The costs shown in table 14 for the pretreatment are the totals for all nine pretreatment batches.

Table 14. Sample cost calculation of yellow grease biodiesel.

Cost Type	Amount	Unit Cost	Cost (\$)	Explanation
Yellow grease	180 kg	0.2865 \$/kg	51.5736	Feedstock cost
Pretreatment				
Methanol	2.502 kg	0.137 \$/kg	0.3447	Stoichiometric
Catalyst (sulfuric acid)	0.999 kg	0.101 \$/kg	0.1008	5% based on FFA amount
Electricity (for pumping)	27 h	0.062 \$/kW–h	0.630	0.373 kW – pump power
Natural gas (for heating)	419.67 kg mixture	0.167 \$/kg (natural gas)	1.197	—
38.475 kg – methanol recovery	1.71 kg natural gas required	0.167 \$/kg (natural gas)	0.279	Excess methanol recovery
	Total for pretreatment of 180 kg feedstock =		54.1251	
Transesterification				
Methanol	16 kg	0.137 \$/kg	2.192	Stoichiometric
Catalyst ($NaOCH_3$)	0.750 kg	1.44 \$/kg	1.08	0.21% based on the oil amount in the feedstock
Electricity (for mixer and pump)	12 h	0.062 \$/kW–h	0.2775	0.373 kW – pump power
Washing water (including disposal fee)	300 kg	0.0010 \$/kg	0.30	—
Heating (for water at 60°C)	300 kg	0.167 \$/kg (natural gas)	0.9869	—
16 kg – methanol recovery	0.481 kg natural gas required	0.167 \$/kg (natural gas)	0.081	Excess methanol was recovered
	Total for transesterification of 180 kg feedstock =		4.9174	For one process
Total overall cost =			59.0425	For one batch
Unit costs =	0.3605 \$/kg	(0.1635 \$/lb)	(1.2006 \$/gal)	For 91% yield

Table 15. Cost comparison of the methyl esters produced in the pilot plant.

Cost Type ($/L)	SME	YGME	BGME
If yield = 99%			
Minimum	0.319	0.190	0.139
Baseline	0.418	0.291	0.221
Maximum	0.518	0.392	0.303
If yield = 91%			
Minimum	—	0.201	0.151
Baseline	—	0.317	0.241
Maximum	—	0.421	0.330

The biodiesel cost comparisons are presented in table 15 for the minimum, baseline, and maximum cases. Although not shown in the table, the effect of varying the FFA level of the feedstock was investigated, but it was found to have only a slight impact on the production cost of biodiesel. A small increase was found because the methanol amount increases in the pretreatment of feedstocks with higher FFA. This also causes more energy cost for the recovery of the excess methanol. However, these are low costs that do not increase the operating cost of the biodiesel from the feedstocks with high FFAs by a large amount.

The consumable costs for biodiesel from both YGME and BGME are considerably less than for SME, primarily because of their lower feedstock cost. Table 15 lists the biodiesel costs assuming that the yield from feedstock is 99%. Currently, the pilot plant shows that a 91% yield is probably a better estimate for YGME and BGME due to interphase losses and washing losses. Estimates with this yield are also listed in table 15. Even with the lower yield assumption, the cost of YGME and BGME was still lower than for SME. State (Iowa) and federal excise taxes on diesel fuel used for on–highway trucks are $0.059/L ($0.225/gal) and $0.064/L ($0.244/gal), respectively. When these are added to the baseline $0.241/L ($0.911/gal) cost of biodiesel from brown grease and a 12% penalty is charged to the biodiesel due to its lower energy content, the cost per equivalent liter (gallon) for BGME biodiesel is $0.41 ($1.55). As mentioned earlier, this cost does not include the capital cost of the plant, labor, transportation, or profit.

CONCLUSIONS

The main objective of this study was to develop a pilot plant to produce methyl esters from soybean oil, yellow grease, and brown grease. Tests were run to confirm that laboratory processes could be scaled up for biodiesel production. To prepare biodiesel from soybean oil, 1% KOH was used as the catalyst with methanol at a 6:1 molar ratio. For yellow grease and brown grease, a two–step acid–catalyzed pretreatment reaction was used to reduce their acid value to less than 2 mg KOH/g. The transesterification reaction was then continued with 0.21% sodium methoxide as the alkaline catalyst.

The following summary statements can be drawn from the experience of designing and operating a pilot plant–scale biodiesel production facility. Some of the conclusions are based on the three case studies that were presented for producing biodiesel from soybean oil, yellow grease with 9% FFA, and brown grease with 40% FFA.

- The results showed that the recipes developed for laboratory–scale biodiesel production could be scaled up to pilot plant–scale if good mixing was maintained. The mixing process is very important in determining the completeness of the transesterification reaction and on the product yield.
- The two–step acid–catalyzed pretreatment process was successful in decreasing the acid values of the yellow grease and brown grease to less than 2 mg KOH/g. After decreasing the acid value of the feedstocks, alkaline–catalyzed transesterification gave good ester conversion, and the biodiesels met the total and free glycerin specifications.
- Glycerin separation is problematic for yellow grease and brown grease and may require water addition. The number of washing cycles is very important and affects the free glycerin amount in the ester produced from pretreated feedstocks with high FFAs.
- The estimated costs for biodiesel from soybean oil, yellow grease, and brown grease were $0.418, $0.317, and $0.241/L, respectively. These costs do not include capital costs or a credit for the value of the co–product glycerin.

ACKNOWLEDGEMENTS

This project was sponsored by a grant for the Iowa Energy Center.

REFERENCES

Aksoy, H. A., I. Kahraman, F. Karaosmanoglu, and H. Civelekoglu. 1988. Evaluation of Turkish sulphur olive oil as an alternative diesel fuel. *JAOCS* 65(6): 936–938.

AOCS. 1991. Official test method Ca 14–56 for total, free. and combined glycerol (iodometric–periodic acid method). In *Official Methods and Recommended Practices of the American Oil Chemists Society.* Champaign, Ill.: AOCS.

______. 1998. Official test method Cd 3a–63 for acid value. In *Official Methods and Recommended Practices of the American Oil Chemists Society.* Champaign, Ill.: AOCS.

Canakci, M. 2001. Production of biodiesel from feedstocks with high free fatty acids and its effect on diesel engine performance and emissions. PhD diss. Ames, Iowa: Iowa State University, Department of Mechanical Engineering.

Canakci, M., and J. Van Gerpen. 1999. Biodiesel production via acid catalysis. *Trans. ASAE* 42(5): 1203–1210.

______. 2001. Biodiesel production from oils and fats with high free fatty acids. *Trans. ASAE* 44(6): 1429–1436.

Chang, D. Y. Z., and J. H. Van Gerpen. 1997. Fuel properties and engine performance for biodiesel prepared from modified feedstocks. SAE Paper No. 971684. Warrendale, Pa.: SAE.

Chang, D. Y. Z., J. H. Van Gerpen, I. Lee, L. A. Johnson, E. G. Hammond, and S. J. Marley. 1996. Fuel properties and emissions of soybean oil esters as diesel fuel. *JAOCS* 73(11): 1549–1555.

Chemical Industry Online. 2000. Website on product costs for Purchasing.com. Available at: www.manufacturing.net/magazine/purchasing. Accessed on 20 October 2000.

Feuge, R. O., E. A. Kraemer, and A. E. Bailey. 1945. Modification of vegetable oils: IV. Reesterification of fatty acids with glycerol. *Oil and Soap* 22: 202–207.

Freedman, B., and E. H. Pryde. 1982. Fatty esters from vegetable oils for use as a diesel fuel. In *Vegetable Oils Fuels: Proc. Int.*

Conf. on Plant and Vegetable Oils as Fuels, 117–122. St. Joseph, Mich.: ASAE.

Freedman, B., E. H. Pryde, and T. L. Mounts. 1984. Variables affecting the yields of fatty esters from transesterified vegetable oils. *JAOCS* 61(10): 1638–1643.

Fuls, J., C. S. Hawkins, and F. J. C. Hugo. 1984. Tractor engine performance on sunflower oil fuel. *J. Agric. Eng. Research* 30(1): 29–35.

Graboski, M. S., and R. L. McCormick. 1998. Combustion of fat and vegetable oil derived fuels in diesel engines. *Prog. Energy Combust. Science* 24(2): 125–164.

Hassett, D. J., and R. A. Hasan. 1982. Sunflower oil methyl ester as diesel fuel. In *Vegetable Oils Fuels: Proc. Int. Conf. on Plant and Vegetable Oils as Fuels*, 123–126. St. Joseph, Mich.: ASAE.

Haumann, B. F. 1990. Renderers give new life to waste restaurant fats. *Inform* 1(8): 722–725.

Hawkins, C. S., and J. Fuls. 1982. Comparative combustion studies on various plant oil esters and the long–term effects of an ethyl ester on a compression ignition engine. In *Vegetable Oils Fuels: Proc. Int. Conf. on Plant and Vegetable Oils as Fuels*, 184–197. St. Joseph, Mich.: ASAE.

Liu, K. 1994. Preparation of fatty acid methyl esters for gas–chromatographic analysis of lipids in biological materials. *JAOCS* 71(11): 1179–1187.

Mittelbach, M., and P. Tritthart. 1988. Diesel fuels derived from vegetable oils: III. Emission tests using methyl esters of used frying oil. *JAOCS* 65(7): 1185–1187.

Nye, M. J., and P. H. Southwell. 1983. Esters from rapeseed oil as diesel fuel. In *Proc. Vegetable Oil as Diesel Fuel – Seminar III*, 78–83. Peoria, Ill.: Northern Agricultural Energy Center.

Peterson, C. L., M. Feldman, R. Korus, and D. L. Auld. 1991. Batch type transesterification process for winter rape oil. *Applied Eng. in Agric.* 7(6): 711–716.

Peterson, C. L., D. L. Reece, B. Hammond, J. C. Thompson, and S. Beck. 1995. Commercialization of Idaho biodiesel (HySEE) from ethanol and waste vegetable oil. ASAE Paper No. 956738. St. Joseph, Mich.: ASAE.

Romano, S. 1982. Vegetable oils – A new alternative. In *Vegetable Oils Fuels: Proc. Int. Conf. on Plant and Vegetable Oils as Fuels*, 106–116. St. Joseph, Mich.: ASAE.

Rudbeck, J. 2000. Market report 1999. *Render* April: 10–14.

Schmidt, K., and J. H. Van Gerpen. 1996. The effect of biodiesel fuel composition on diesel combustion and emissions. SAE Paper No. 961086. Warrendale, Pa.: SAE.

Schumacher, L. G., and J. H. Van Gerpen. 1996. Research needs resulting from experiences of fueling of diesel engines with biodiesel. In *Liquid Fuels and Industrial Products from Renewable Resources: Proc. 3rd Liquid Fuel Conference*, 207–216. St. Joseph, Mich.: ASAE.

Sharp, C. A. 1998. Characterization of biodiesel exhaust emissions for EPA 211(b). Final report for National Biodiesel Board. San Antonio, Texas: Southwest Research Institute.

USDA. 2000. Website for the USDA Economic Research Service. Available at: www.ers.usda.gov. Accessed on 20 Oct. 2000.

Van Gerpen, J. H., E. G. Hammond, L. Yu, and A. Monyem. 1997. Determining the influence of contaminants on biodiesel properties. SAE Paper No. 971685. Warrendale, Pa.: SAE.

Zhang, Y., and J. H. Van Gerpen. 1996. Combustion analysis of esters of soybean oil in a diesel engine. SAE Paper No. 960765. Warrendale, Pa.: SAE.