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Production of biodiesel from feedstocks with high free fatty acids and its effect on diesel engine performance and emissions

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Production of biodiesel from feedstocks with high free fatty acids and its effect on diesel engine performance and emissions

by

Mustafa Canakci

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY

Major: Mechanical Engineering
Major Professor: Jon H. Van Gerpen

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ABSTRACT

Biodiesel is a fuel consisting of the alkyl monoesters of fatty acids from vegetable oils or animal fats. Biodiesel is receiving increasing attention as an alternative, non-toxic, biodegradable and renewable diesel fuel. Many studies have shown that the properties of biodiesel are very close to diesel fuel. Therefore, biodiesel can be used in diesel engines with little or no modification.

Biodiesel is usually produced from food-grade vegetable oils that are more expensive than diesel fuel. Therefore, use of biodiesel produced from food-grade vegetable oil may be limited to cases of severe shortages or emergencies. However, lower cost feedstocks are available. Rendered animal fats and restaurant waste oils are an attractive source to produce biodiesel. The problem with processing rendered fats and oils is that they usually contain large amounts of free fatty acids that cannot be converted to biodiesel using an alkaline catalyst due to the formation of soaps. An alternative way is to use acid catalysts, which are more tolerant of free fatty acids.

The objective of this study was to develop a process to utilize rendered fats, known as yellow grease, as a biodiesel feedstock and to build a pilot plant to implement this process. The pilot plant was successfully constructed and was shown to be capable of processing rendered fats containing 40% free fatty acids.

After preparing a sufficient amount of biodiesel from rendered animal fats and restaurant waste oils, the impact of the biodiesel on diesel engine exhaust emissions and engine performance was evaluated and compared to No. 2 diesel fuel and soybean oil methyl ester. The methyl esters produced from yellow grease gave nearly the same thermal efficiency but higher fuel consumption compared with No. 2 diesel fuel. At the operating condition studied, the biodiesel produced 17.77% and 46.27% lower CO and HC emissions, respectively, than No. 2 diesel fuel. The Bosch Smoke Number for biodiesel from yellow grease was 64.21% less than with No. 2 diesel fuel. The methyl esters had 11.60% higher NO_x emissions than the No. 2 diesel fuel. No significant differences were found in the exhaust emissions and engine performance between the biodiesel produced from yellow grease and biodiesel from soybean oil.

1. INTRODUCTION

Rudolph Diesel, a German engineer, introduced the diesel engine over a century ago [1]. Since then a great deal of research and development has taken place not only in the design area but also in 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.

The alkyl monoesters of fatty acids from vegetable oils and animal fats, known as *biodiesel,* are receiving increasing attention as an alternative, non-toxic, biodegradable and renewable diesel fuel. Many studies have shown that the properties of biodiesel are very close to diesel fuel. Therefore, biodiesel fuel can be used in diesel engines with little or no modification. Biodiesel has a higher cetane number than diesel fuel, no aromatics, 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 diesel fuel.

In Europe, a specific type of biodiesel called rapeseed methyl ester (RME) is widely used as a fuel source. Only recently has the United States considered these non-petroleum oils to be a reasonable source of alternative fuel. The low volatility and high cetane number of vegetable oils and their derivatives render them better suited for use in diesel engines than spark-ignited engines [2, 3].

Many researchers have concluded that vegetable oils hold promise as alternative fuels for diesel engines [4, 5]. However, using raw vegetable oils for diesel engines can cause numerous engine-related problems [6, 7]. The increased viscosity and low volatility of vegetable oils lead to severe engine deposits, injector coking, and piston ring sticking [8-11]. However, these effects can be reduced or eliminated through transesterification of the vegetable oil to form a methyl ester [8, 12]. The process of transesterification removes glycerin from the triglycerides and replaces it with radicals from the alcohol used for the conversion process [13, 14]. This process decreases the viscosity but maintains the cetane number and the heating value.

One drawback of biodiesel is that there is a tradeoff between biodiesel's level of saturation and its cold flow properties. Table 1.1 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. Biodiesel from soybean oil is highly unsaturated so its cold flow properties are acceptable, however it is more prone to oxidation. The impact of this oxidation on the engine's performance and emissions is not currently understood.

Over the past 7 years, considerable research has been conducted to investigate the properties of biodiesel, its performance in engines, and to provide the supporting data needed to satisfy the Environmental Protection Agency's Fuels and Fuel Additives Registration

Table 1.1: Fatty acid distribution of some vegetable oils and animal fats

Product	***Fatty Acid Distribution (% by weight)***							***Saturation Level (%)***	***Ref. No.***
	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	5
Sunflower Oil	-	6.08	-	3.26	16.93	73.73	-	9.34	5
Safflower Oil	-	8.60	-	1.93	11.58	77.89	-	10.53	5
Soybean Oil	-	10.58	-	4.76	22.52	52.34	8.19	15.34	*
Lard	1-2	28-30	-	12-18	40-50	7-13	-	41-50	15
Tallow	3-6	24-32	-	20-25	37-43	2-3	-	47-63	15
Yellow Grease	2.43	23.24	3.79	12.96	44.32	6.97	0.67	38.63	*
Brown Grease	1.66	22.83	3.13	12.54	42.36	12.09	0.82	37.03	*

*Measured by Woodson-Tenent Laboratories, Inc., Des Moines, IA.

program [16-20]. Virtually all of this work is based on the methyl ester of soybean oil. Soybean oil was chosen because, in the United States, soybean oil is the only oil that is available in sufficient quantity to supply a national market. However, the cost of food-grade soybean oil limits its use in diesel engines. Therefore, biodiesel from food grade vegetable oil can be used only in cases of severe shortages or emergency. Reducing the cost of the feedstock is necessary for biodiesel to be commercially viable.

Waste vegetable oil from restaurants and rendered animal fats are inexpensive compared with food-grade vegetable oil. Approximately 2.5 billion pounds of waste restaurant fats are collected annually from restaurants and fast-food establishments in the U.S. [21]. The problem with processing waste oils is that they usually contain large amounts of free fatty acids that cannot be converted to biodiesel using an alkaline catalyst due to formation of soaps. The soaps can prevent separation of the biodiesel from the glycerin fraction. An alternative method is to use acid catalysts which some researchers have claimed are more tolerant of free fatty acids [22-24]. A significant number of research studies have been conducted related to the esterification of vegetable oils with different alkaline catalysts.

However, there have been only a few studies about esterification with acid catalysts.

The properties of biodiesel vary somewhat depending on the oil feedstock and alcohol used but are always very close to diesel fuel [25-27]. The American Society for Testing and Materials (ASTM) is currently developing a standard for biodiesel. The proposed standard is based on the specifications developed by the National Biodiesel Board shown in Table 1.2 [28]. The objective of this standard is to have biodiesel meet the performance requirements of engines without specifying the actual composition of the fuel. This will allow biodiesel to be made from any feedstock as long as the standard can be met. This is the approach currently used with petroleum-based diesel fuel.

The primary objective of this project was to investigate the use of low-cost, high free fatty acid feedstocks to produce commercially viable biodiesel. To accomplish this objective the following tasks were identified.

- Develop a technique to convert high free fatty acid feedstocks to fuel quality biodiesel.
- Implement the biodiesel production technique in a pilot plant.
- Compare the performance and emissions of a diesel engine fueled with biodiesel from high free fatty acid feedstocks with biodiesel from soybean oil and with petroleum-based diesel fuel.

Table 1.2: The National Biodiesel Board specifications for biodiesel [28]

Property	*ASTM Method*	*Limits*	*Units*
Flash Point	D 93	100 min	°C
Water and Sediment	D 1796	0.050 max	Vol. %
Carbon Residue, 100% sample	D 4530	0.050 max	wt %
Sulfated Ash	D 874	0.020 max	wt %
Kinematic Viscosity, 40°C	D 445	1.9 - 6.0	mm^2/sec
Sulfur	D 2622	0.05 max	wt %
Cetane Number	D 613	40 min	-
Cloud Point	D 2500	By customer	°C
Copper Strip Corrosion	D 130	No. 3b max	-
Acid Number	D 664	0.80 max	mg KOH/g
Free Glycerin	GC*	0.020 max	wt %
Total Glycerin	GC*	0.240 max	wt %

* Method by C. Plank [29]

2. REVIEW OF LITERATURE

This chapter includes the background information on biodiesel as well as a review of the relevant literature. The first two sections present the information about vegetable oils and transesterification. Next two sections discuss the transesterification of the oils and fats with high free fatty acids in small scale and large-scale production. Then, the potential of the rendered animal fat and restaurant waste oils in the United States and Iowa is presented. This is followed by a discussion of the chemical properties of the rendered animal fat and restaurant waste oils. Finally, diesel engine emissions from biodiesels produced from different feedstocks will be discussed.

2.1. Vegetable Oils

In the 1930s and 1940s, vegetable oils were used as emergency fuels [30]. These oils contain no sulfur but have about 10% oxygen, by weight. This tends to reduce their carbon monoxide, unburned hydrocarbons, sulfur dioxide, and particulate emissions when compared to diesel fuel. Therefore, using vegetable oil-based fuels may reduce air pollution.

Vegetable oils are fatty esters of glycerin (triglycerides) and have the chemical structure shown in Figure 2.1 [31]: where R_1, R_2, and R_3 represent the hydrocarbon chain of the fatty acids. R_1, R_2, and R_3 depend on the particular oil, but for vegetable oils and animal fats usually contain 16-18 carbons and from 0 to 3 double bonds. The term *oil* is generally used for triglycerides that are liquid at ambient temperature and *fat* is used when the triglycerides are solid.

Although many of the properties of vegetable oil are similar to diesel fuel, the viscosity of the vegetable oil is much higher. Due to the high viscosity of the vegetable oils,

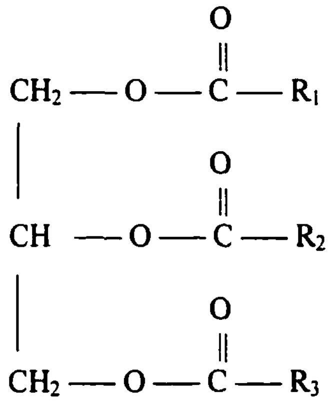


Figure 2.1: Chemical structure of a triglyceride

problems such as injector coking, piston ring sticking, and thickening of the lubricating oil have arisen when engines have been fueled with vegetable oils [32-36].

2.2. Transesterification

One approach to reducing the viscosity of vegetable oils is transesterification. Transesterification is a chemical process of reacting vegetable oils with alcohol in the presence of a catalyst as shown in Figure 2.2.

The monoesters produced by transesterification of vegetable oils or animal fats are known as *biodiesel*. Transesterification significantly reduces the viscosity of vegetable oils without affecting the heating value of the original fuel. Therefore, fuel atomization, combustion, and emission characteristics will display better results than pure vegetable oil if the esters of vegetable oils are used in engines. Alcohols such as ethanol, methanol, or butanol can be used in the transesterification and the monoesters are named methyl esters, ethyl esters, or butyl esters, respectively.

The catalysts used in transesterification are generally classified in two categories, acidic and alkaline. The most commonly preferred acid catalysts are sulfuric, sulphonic, and

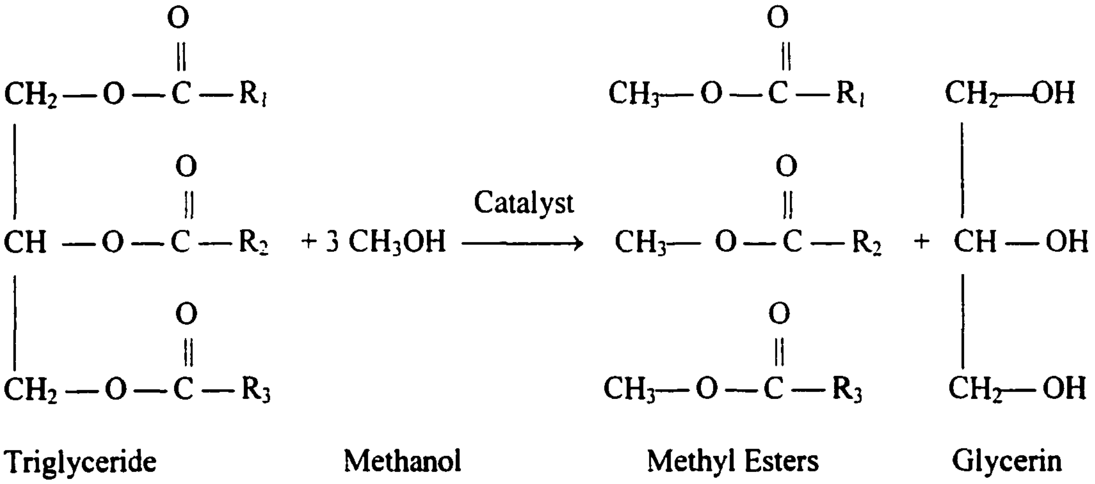


Figure 2.2: Transesterification of triglyceride using methanol and catalyst

hydrochloric acids and sodium hydroxide, sodium methoxide, and potassium hydroxide are preferred as alkaline catalysts.

The residue of the catalyst in the ester may cause some engine problems. In particular, acid catalysts will attack metallic engine parts and alkaline catalysts produce solid ash particles during combustion. Therefore, the catalyst in the ester must be removed from the fuel when the reaction is complete. This is usually done by washing the ester with water. Feuge and Gros [37] investigated the effect of catalyst amount, ethanol concentration, and temperature on the transesterification of peanut oil. They used sodium hydroxide as a catalyst. To obtain the effect of catalyst and ethanol concentration on the free glycerin yield, they selected five different combinations of alcohol/oil molar ratio and catalyst percentage at a constant temperature of 50°C. After running each test for about 200 minutes, they found that a stoichiometric molar ratio of alcohol to oil and 0.2% catalyst yielded the minimum glycerin and a molar ratio of 2 times the stoichiometric amount of alcohol to oil and 0.8% catalyst gave the maximum glycerin amount or the most complete reaction. To determine the effect of temperature, three temperature levels (30°C, 50°C, and 70°C) were selected. By using 2 times the stoichiometric amount of alcohol/oil ratios and 0.2% catalyst percentages, the variation of glycerin with temperature was found after 16 hours of reaction time. The glycerin yields were 86% and 91% at 30°C and 50°C, respectively. During the first few minutes of the reaction the rate of alcoholysis was greatest at 70°C. However, the optimum temperature for glycerin yield from peanut oil with ethanol was found to be 50°C and the lowest yield was at 70°C. The authors did not suggest a reason for this result.

Formo [38] published a review about the acid catalyzed ester reactions of fatty materials. Formo states that the methyl esters can be prepared from fatty acids by using a large excess of methanol (15 to 35 moles per mole of fatty acid) and sulfuric acid as a catalyst. After refluxing (a reaction at the alcohol's boiling temperature but where vaporized alcohol is condensed and returned to the reaction) for several hours, ester yields of 95% or higher can be obtained.

Hartman [39] investigated six different alkali catalysts at 60°C and reflux conditions to determine the most effective catalyst on ox fat, coconut oil, and linseed oil after neutralizing the oils with sodium hydroxide, washing, and drying in vacuum. The reaction mixtures were acidified with acetic acid and then the esters were extracted with ethyl ether and washed with water. After two hours of reaction time, sodium methoxide and ignited potassium carbonate were found to set free 99-99.5% of the total glycerin and cause the least degree of saponification (sodium or potassium from the catalyst combining with free fatty acids to form soaps). The amounts of the catalysts were 0.5% and 10.0% for sodium methoxide and ignited potassium carbonate, respectively.

Luddy et al. [40] studied the production of methyl esters from the lipids of plasma, cells, liver, and soybeans using potassium methoxide as a catalyst. They reported that 92-96% conversion to methyl ester could be obtained with methanolysis (the transesterification reaction of the added alcohol, methanol). They also compared the effect of the amount and concentration of sodium methoxide catalyst and the reaction time on the yield of methyl esters from cholesterol esters. The effectiveness of sodium methoxide and potassium methoxide on methanolysis was also compared in this paper. Potassium methoxide was found to be more effective and produced greater conversion to methyl esters than sodium methoxide.

Gauglitz and Lehman [41] studied straight- and branched-chain alcohols having 1-6 carbon atoms in esterification reactions. Ethyl, methyl, n-propyl, i-propyl, n-butyl, i-butyl, and n-hexyl esters were prepared at the same conditions. In that research they esterified highly unsaturated fish oil using metallic sodium dissolved in the alcohols as a catalyst. They found that the conversion of straight-chain esters was a linear function of the number of carbon atoms in the alcohol. No reaction was observed when t-butyl alcohol was used. The reaction times varied from 2 minutes for methanol to 60 minutes for n-hexanol. Branched-chain alcohols (such as isopropyl alcohol) were found to react more slowly than straight-chain alcohols (such as methanol).

McGinnis and Dugan [42] compared three methods for preparing methyl esters of different fatty acids. The methods were a base-catalyzed interesterification method, a saponification and esterification method, and a low temperature sulfuric acid method. They concluded that the low temperature sulfuric acid method has some advantages compared to the other two methods. It directly converts the fatty acid component to methyl esters without the need for saponification and isolation of the fatty acids. In this respect it resembles base-catalyzed interesterification. Another advantage of the low temperature sulfuric acid method is that it does not promote any conjugation of double bonds. Conjugation of double bonds can occur under the conditions of base-catalyzed interesterification and results in esters that are more prone to oxidation.

Freedman and Pryde [23] investigated the effects of reaction variables on transesterification using sunflower and soybean oils. They studied different molar ratios of alcohol to oil, alcohol types, catalyst types, and reaction temperature. In that study, ester conversions of 90 to 97% were obtained by using alcohol to oil molar ratios of 4:1 and 6:1, respectively, with an alkaline catalyst. Below the theoretical ratio (3:1), the residual levels of tri-, di-, and monoglycerides were found to increase. When using methyl, ethyl, and butyl alcohol to esterify sunflower oil, the percentages of methyl, ethyl and butyl esters were 98%, 96%, and 96%, respectively, after a 1-hour reaction period. They also compared two catalysts (sodium hydroxide and sodium methoxide) at 6:1 and 3:1 molar ratios and found that sodium methoxide (0.5%) was more effective than sodium hydroxide (1%) at the 3:1 molar ratio. At the 6:1 molar ratio, the catalysts were equally effective.

Freedman and Pryde [23] also used sulfuric acid to transesterify soybean oil. A 30:1 molar ratio of methanol to soybean oil with 1% sulfuric acid gave good conversion after 44 hours of heating at 60°C. Butyl alcohol with 1% sulfuric acid converted the oil to 98% ester after 4 hours of heating at 114°C. They emphasized that if vegetable oil has more than 1% free fatty acids, the free fatty acids will destroy an alkali catalyst where an acid catalyst would still be effective. To investigate the effect of temperature, a mixture of 6:1 molar ratio of methanol to soybean oil with 1% sodium hydroxide was reacted at temperatures of 32°C, 45°C, and 60°C. After 1 hour of reaction time, the 45°C and 60°C conditions gave 97% ester but the 32°C condition gave a slightly lower conversion of 92%.

Nye et al. [43] performed a study to produce methyl esters from used frying oil. After filtering, the free fatty acid content of the used frying oil was measured to be 1.5%, which is actually quite low and not a good test of the technology needed to utilize waste oils. Methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-ethoxyethanol were evaluated as alcohols and sulfuric acid (0.1%) and potassium hydroxide (0.4%) were evaluated as acid and base catalysts, respectively. The highest ester productions at 25°C were found with 1-butyl ester with an acid catalyst, which gave 81% conversion, methyl ester with a base catalyst, which gave 74% conversion, and ethyl ester with an acid catalyst, which gave 72% conversion.

Freedman and co-workers [44] investigated the variables that affect ester formation from cottonseed, peanut, soybean, and sunflower oils. They reported the effects of molar ratio of alcohol to vegetable oil, of temperature, and of the type of catalyst (base or acidic). They stressed that the yields of ester were reduced significantly if some reaction conditions did not meet certain requirements such as an acid value less than 1 mg KOH/g and alcohol and vegetable oil that are moisture free. The molar alcohol to oil ratio was varied from 1:1 to 6:1 and the highest conversion was obtained at the 6:1 molar ratio, which gave 98%. The other oils also showed similar behavior at varying molar ratios and the highest yields of ester were between 93% and 98%. In that study, the effect of temperature on the ester yield was also monitored. They studied a 6:1 molar ratio of methanol to soybean oil with 1% sodium hydroxide catalyst at three temperature levels, 60°C, 45°C, and 32°C. After 0.1 hour, the ester formations were 94%, 87%, and 64%, respectively. However, they noted that identical amounts of esters were converted at the three temperature levels after 1 hour of reaction time.

They also compared acid (sulfuric acid) and base (sodium hydroxide) catalysis. For this experiment, 6:1, 20:1, and 30:1 molar ratios were selected to characterize acid catalysis. The molar ratios of 6:1 and 20:1 gave unsatisfactory ester conversion even after 18 hours of reaction time. The highest conversion (no number was given) with the acid catalyst was found at the 30:1 molar ratio. Samples of 30:1 molar ratio of alcohol to soybean oil with 1% acid catalyst were investigated at three temperatures. The temperatures selected were a few degrees below the boiling temperatures of the alcohols, 65°C, 78°C, and 117°C for methyl, ethyl, and butyl alcohol, respectively. They found the ester conversions reached a maximum after 3, 22, and 69 hours for butyl, ethyl, and methyl alcohol, respectively, but the transesterification reaction by acid catalysis was much slower than by base catalysis.

Nye and Southwell [45] have reported the results of several important reaction parameters on the methyl and ethyl esters of rapeseed oil at room temperature conditions. Catalyst type and concentration and molar ratio were identified as the primary reaction variables. They tested the following catalysts: magnesium and calcium oxides and carbonates, basic and acidic macroreticular organic resins, alkaline alumina, sodium and potassium hydroxides and alkoxides, phase transfer catalysts, sulfuric acid, p-toluenesulfonic acid, and dehydrating agents as co-catalysts. They concluded that only alkoxides and hydroxides were effective at room temperature. Using a 6:1 molar ratio of methanol to rapeseed oil with 1% sodium hydroxide gave the maximum amount of ester for the molar ratios studied.

Freedman et al. [46] studied transesterification kinetics of soybean oil by using various types of catalysts. By using a computer-modeling program, they calculated the rate constants of the reactions of butyl alcohol with soybean oil for a 6:1 molar ratio at different temperature and catalyst conditions. They concluded that the rate constants for the alkaline-catalyzed reactions were much larger than for the acid-catalyzed reactions.

As with many earlier researchers, Schwab and co-workers [47] found that molar ratio, temperature, and catalyst type were the main variables in transesterification. In their review, it was also noted that the highest ester yield was obtained at twice that required by the stoichiometry of the mixture of methanol and soybean oil with 0.5% sodium methoxide at 60°C. They emphasized that alkali-catalyzed transesterification converts faster compared to acid-catalyzed transesterification. One percent sodium hydroxide as a catalyst showed a stronger effect than 0.5% sodium methoxide. They concluded that, when given enough time, vegetable oils can be transesterified satisfactorily with sodium hydroxide at ambient temperature.

Liu [24] has also noted that there are many potential catalysts, and characterized the most common as acidic (HCl, H_2SO_4, and BF_3) and alkaline ($NaOCH_3$, KOH, and NaOH). Liu compared the catalysts and noted that acid catalysis can esterify triglycerides and other complex lipids and free fatty acids in alcohol. Heating is required for faster reaction and the reaction time may vary from a few minutes to several hours. He mentioned that although boron fluoride alcoholate has higher esterifying capability, it is toxic and expensive. It also has a limited shelf life. Sulfuric acid-methanol solution (H_2SO_4/MeOH) is preferred to hydrochloric acid-methanol solution (HCl/MeOH) because of its easy preparation. Liu also mentioned that base catalysts are much faster than acid catalysts. However, they are unable to esterify free fatty acids so Liu concluded that the acid value of the oil or fat should be less than 2 mg KOH/g.

Muniyappa et al. [48] studied esterification of plant oils and animal fats for fuel purposes. In their work, the objective was to optimize the catalyst concentration and reaction time without reduction of the transesterification yield of soybean oil. Sodium hydroxide was used as a catalyst and its effect was investigated by changing its concentration from 0.5 to 0.05% in a 30:1 molar ratio of methanol to soybean oil. They noted that the catalyst concentration did not have a significant effect on the conversion. All reactions were run at about 68-70°C, with a 90-minute reaction time, and with soybean oil having an acid value less than 0.05 mg KOH/g. They found that 98% conversion could be obtained with 0.1% catalyst after only 5-10 minutes of reaction time.

Boocock et al. [49, 50] have developed a new method which forms methyl esters in less time than traditional methods. They found that simple ethers, such as tetrahydrofuran (THF), which was the best found so far, and methyl tertiary butyl ether (MTBE) could be used as cosolvents for the alcohol and oil and caused faster transesterification. They used the following methods. Vegetable oil and anhydrous THF were mixed together and sodium hydroxide solution in methanol was added to the mixture while stirring. Adding an amount of THF equal to approximately 1.25 times the volume of methanol caused a modest increase in the total volume of the mixture, but a significant reduction in reaction time occurred at a methanol to oil molar ratio of 6:1 using 1.0 wt% sodium hydroxide catalyst and a temperature of 23°C. Boocock found that 95.0 wt% methyl ester was formed in 20 minutes. They extended their study for four different sodium hydroxide catalyst concentrations for a 6:1 molar ratio. The ester contents after 1 minute for 1.1, 1.3, 1.4 and 2.0 wt% (based on the oil) sodium hydroxide were 82.5, 85.0, 87.0, and 96.2 %, respectively. When the methanol to oil ratio was varied from 25:1 to 40:1 for 1% sodium hydroxide catalyst, the ester conversions were 94.7, 98.3, 98.0, 96.2, and 95.0% after 5 minutes for 25:1, 27:1, 28:1, 35:

1, and 40:1 molar ratios, respectively. However, the highest ester conversion was 99.4 wt% at the molar ratio of 27:1 after 7 minutes. At 40:1 molar ratio, the conversion was 95 wt% after 5 minutes while the 27:1 molar ratio gave 98.3 wt% in the same reaction time.

Table 2.1 summarizes the effects of the molar ratio, catalyst type and amount, alcohol type and amount, and temperature on the ester conversion for small scale transesterification processes.

2.3. The Transesterification of Oils and Fats with High Free Fatty Acids

Biodiesel is currently produced from food-grade vegetable oils that are more expensive than diesel fuel. However, lower cost feedstocks are available, specifically waste vegetable oils and fats. 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* and if it is above 15% it is called *brown grease*.

Some researchers [51-55] have focused on the use of rendered animal fats and restaurant waste oils as diesel fuel extenders. However, the amount of oil that can be added to the diesel fuel is limited by the same concerns discussed earlier for refined oils. Rendered animal fats and restaurant waste oils are an attractive source to produce biodiesel. There are large amounts of waste vegetable oils from the food industry that could be converted to biodiesel. This section reviews previous work on the production of biodiesel from rendered animal fats and restaurant waste oils with high FFA levels.

To prepare esters with a high yield, it is necessary for the feedstock to have a low acid value. The acid value is a measure of the number of acidic functional groups in a sample and is measured in terms of the quantity of a powerful base (potassium hydroxide) required to

Table 2.1: Summary of the small scale transesterification processes

Type and Amount of Oil and Alcohol (Molar Ratio)	*Catalyst*	*Temp. (°C)*	*Reaction Time*	*Conversion (%)*	*Ref. No.*
Peanut oil & ethanol (1:2)	Sodium hydroxide (0.2%)	30	16 Hours	86.0	37
Peanut oil & ethanol (1:2)	Sodium hydroxide (0.2%)	50	16 Hours	91.0	37
Peanut oil & ethanol (1:2)	Sodium hydroxide (0.2%)	70	16 Hours	<86.0	37
Ox fat & methanol (25% Methanol, as wt.)	$NaOCH_2$ (0.5%)	60	2 Hours	99.39	39
Ox fat & methanol (25% Methanol, as wt.)	NaOH (0.5%)	60	4 Hours	97.84	39
Ox fat & methanol (25% Methanol, as wt.)	K_2CO_3 (10.0%)	Reflux	2 Hours	99.35	39
Ox fat & methanol (25% Methanol, as wt.)	CaO (1.5%)	Reflux	8 Hours	97.25	39
Ox fat & methanol (25% Methanol, as wt.)	BaO (1.5%)	Reflux	8 Hours	82.94	39
Ox fat & methanol (25% Methanol, as wt.)	SrO (1.5%)	Reflux	8 Hours	70.30	39
Coconut oil & methanol (25% Methanol, as wt.)	$NaOCH_2$ (0.5%)	60	2 Hours	99.41	39
Coconut oil & methanol (25% Methanol, as wt.)	NaOH (0.5%)	60	4 Hours	98.02	39
Coconut oil & methanol (25% Methanol, as wt.)	K_2CO_3 (10.0%)	Reflux	2 Hours	98.92	39
Coconut oil & methanol (25% Methanol, as wt.)	CaO (1.5%)	Reflux	8 Hours	96.50	39
Coconut oil & methanol (25% Methanol, as wt.)	BaO (1.5%)	Reflux	8 Hours	89.26	39
Coconut oil & methanol (25% Methanol, as wt.)	SrO (1.5%)	Reflux	8 Hours	78.41	39
Linseed oil & methanol (25% Methanol, as wt.)	$NaOCH_2$ (0.5%)	60	2 Hours	99.24	39
Linseed oil & methanol (25% Methanol, as wt.)	NaOH (0.5%)	60	4 Hours	98.11	39
Linseed oil & methanol (25% Methanol, as wt.)	K_2CO_3 (10.0%)	Reflux	2 Hours	99.32	39
Linseed oil & methanol (25% Methanol, as wt.)	CaO (1.5%)	Reflux	8 Hours	96.87	39
Linseed oil & methanol (25% Methanol, as wt.)	BaO (1.5%)	Reflux	8 Hours	89.93	39
Linseed oil & methanol (25% Methanol, as wt.)	SrO (1.5%)	Reflux	8 Hours	75.54	39
Sunflower Oil & methanol (1:1)	Sodium methoxide (0.5%)	60	1 Hour	35.0	47
Sunflower Oil & methanol (1:2)	Sodium methoxide (0.5%)	60	1 Hour	68.0	47
Sunflower Oil & methanol (1:3)	Sodium methoxide (0.5%)	60	1 Hour	82.0	47

Table 2.1: continued

Type and Amount of Oil and Alcohol (Molar Ratio)	*Catalyst*	*Temp. (°C)*	*Reaction Time*	*Conversion (%)*	*Ref. No.*
Sunflower Oil & methanol (1:4)	Sodium methoxide (0.5%)	60	1 Hour	90.0	47
Sunflower Oil & methanol (1:5)	Sodium methoxide (0.5%)	60	1 Hour	93.0	47
Sunflower Oil & methanol (1:6)	Sodium methoxide (0.5%)	60	1 Hour	98.0	47
Sunflower Oil & methanol (1:6)	Sodium methoxide (0.5%)	60	1 Hour	98.0	23, 44
Sunflower Oil & ethanol (1:6)	Sodium methoxide (0.5%)	75	1 Hour	96.0	23, 44
Sunflower Oil & butanol (1:6)	Sodium methoxide (0.5%)	114	1 Hour	96.0	23, 44
Sunflower Oil & ethanol (1:3)	Sodium methoxide (0.5%)	75	1 Hour	81.0	44
Sunflower Oil & butanol (1:3)	Sodium methoxide (0.5%)	114	1 Hour	88.0	44
Sunflower Oil & methanol (1:3)	Sodium methoxide (0.5%)	60	1 Hour	82.0	23, 44
Soybean Oil & methanol (1:3)	Sodium hydroxide (1.0%)	60	1 Hour	~62.0	23, 44
Soybean Oil & methanol (1:6)	Sodium hydroxide (1.0%)	60	1 Hour	97.0	23, 44
Soybean Oil & methanol (1:6)	Sodium hydroxide (1.0%)	45	1 Hour	97.0	23, 44
Soybean Oil & methanol (1:6)	Sodium hydroxide (1.0%)	32	1 Hour	92.0	23, 44
Soybean Oil & methanol (1:6)	Sodium hydroxide (1.0%)	32	4 Hours	99.0	23
Used frying oil & methanol (1:3.6)	Potassium hydroxide (0.4%)	50	24 Hours	73.8	43
Used frying oil & methanol (1:3.6)	Sulfuric acid (0.1%)	~65	40 Hours	52.7	43
Used frying oil & ethanol (1:3.6)	Potassium hydroxide (0.4%)	50	24 Hours	46.1	43
Used frying oil & ethanol (1:3.6)	Sulfuric acid (0.1%)	~73	40 Hours	72.0	43
Used frying oil & 1-propanol (1:3.5)	Potassium hydroxide (0.4%)	50	24 Hours	31.9	43
Used frying oil & 1-propanol (1:3.5)	Sulfuric acid (0.1%)	~90	40 Hours	53.9	43
Used frying oil & 2-propanol (1:3.5)	Potassium hydroxide (0.4%)	50	24 Hours	2.2	43
Used frying oil & 2-propanol (1:3.5)	Sulfuric acid (0.1%)	~80	40 Hours	48.3	43

Table 2.1: continued

Type and Amount of Oil and Alcohol (Molar Ratio)	*Catalyst*	*Temp. (°C)*	*Reaction Time*	*Conversion (%)*	*Ref. No.*
Used frying oil & 1-butanol (1:3.6)	Potassium hydroxide (0.4%)	50	24 Hours	47.7	43
Used frying oil & 1-butanol (1:3.6)	Sulfuric acid (0.1%)	~105	40 Hours	81.3	43
Used frying oil & 2-exhoxyethanol (1:3.5)	Potassium hydroxide (0.4%)	50	24 Hours	29.4	43
Used frying oil & 2-exhoxyethanol (1:3.5)	Sulfuric acid (0.1%)	~125	40 Hours	47.5	43
Soybean Oil & methanol (1:6)	Sulfuric acid (1.0%)	60	1 Hours	~0	23
Soybean Oil & methanol (1:30)	Sulfuric acid (1.0%)	60	44 Hours	good	23
Soybean Oil & butanol (1:30)	Sulfuric acid (1.0%)	114	44 Hours	98	23
Soybean Oil & methanol (1:6)	Sulfuric acid (1.0%)	65	3 Hours	unsatisfactory	44
Soybean Oil & ethanol (1:6)	Sulfuric acid (1.0%)	78	3 Hours	unsatisfactory	44
Soybean Oil & butanol (1:6)	Sulfuric acid (1.0%)	117	3 Hours	unsatisfactory	44
Soybean Oil & methanol (1:20)	Sulfuric acid (1.0%)	65	18 Hours	unsatisfactory	44
Soybean Oil & ethanol (1:20)	Sulfuric acid (1.0%)	78	18 Hours	unsatisfactory	44
Soybean Oil & butanol (1:20)	Sulfuric acid (1.0%)	117	18 Hours	unsatisfactory	44
Soybean Oil & methanol (1:30)	Sulfuric acid (1.0%)	65	69 Hours	~98	44
Soybean Oil & ethanol (1:30)	Sulfuric acid (1.0%)	78	22 Hours	~98	44
Soybean Oil & butanol (1:30)	Sulfuric acid (1.0%)	117	3 Hours	~98	44
Soybean Oil & methanol (1:30)	Sulfuric acid (1.0%)	65	69 Hours	~98	44
Soybean Oil & ethanol (1:30)	Sulfuric acid (1.0%)	65	69 Hours	~98	44
Soybean Oil & butanol (1:30)	Sulfuric acid (1.0%)	65	69 Hours	~98	44
Soybean Oil, methanol &THF (1:6) (THF 1.25 times the vol. of methanol)	sodium hydroxide (1.0%)	23	20 min.	95.0	50
Soybean Oil, methanol &THF (1:6) (THF 1.25 times the vol. of methanol)	sodium hydroxide (1.1%)	23	1 min.	82.5	50
Soybean Oil, methanol &THF (1:6) (THF 1.25 times the vol. of methanol)	sodium hydroxide (1.3%)	23	1 min.	85.0	50

Table 2.1: continued

Type and Amount of Oil and Alcohol (Molar Ratio)	*Catalyst*	*Temp. (°C)*	*Reaction Time*	*Conversion (%)*	*Ref. No.*
Soybean Oil, methanol &THF (1:6) (THF 1.25 times the vol. of methanol)	sodium hydroxide (1.4%)	23	1 min.	87.0	50
Soybean Oil, methanol &THF (1:6) (THF 1.25 times the vol. of methanol)	sodium hydroxide (2.0%)	23	1 min.	96.2	50
Soybean Oil, methanol &THF (1:6) (THF 1.25 times the vol. of methanol)	sodium hydroxide (2.0%)	23	3 min.	98.8	50
Soybean Oil, methanol &THF (1:6) (THF 1.25 times the vol. of methanol)	sodium hydroxide (1.3%)	23	15 min.	95.0	50
Soybean Oil, methanol &THF (1:25) (THF 1.25 times the vol. of methanol)	sodium hydroxide (1.0%)	23	5 min.	94.7	50
Soybean Oil, methanol &THF (1:27) (THF 1.25 times the vol. of methanol)	sodium hydroxide (1.0%)	23	5 min.	98.3	50
Soybean Oil, methanol &THF (1:28) (THF 1.25 times the vol. of methanol)	sodium hydroxide (1.0%)	23	5 min.	98.0	50
Soybean Oil, methanol &THF (1:35) (THF 1.25 times the vol. of methanol)	sodium hydroxide (1.0%)	23	5 min.	96.2	50
Soybean Oil, methanol &THF (1:40) (THF 1.25 times the vol. of methanol)	sodium hydroxide (1.0%)	23	5 min.	95.0	50
Soybean Oil, methanol &THF (1:27) (THF 1.25 times the vol. of methanol)	sodium hydroxide (1.0%)	23	7 min.	99.4	50
Soybean Oil, methanol &THF (1:28) (THF 1.25 times the vol. of methanol)	sodium hydroxide (1.0%)	23	7 min.	99.2	50

neutralize the sample. It is different from the pH of the sample in that it does not measure the strength of the acids. The percentage of FFAs in most vegetable oils and animal fats can be estimated by dividing the acid value in half, i.e. 1 mg KOH/g is equivalent to 0.5% FFA.

With traditional alkali catalyzed processes, free fatty acids escape conversion into esters by reacting with the catalyst to form soaps. With acid catalyzed processes, the reaction of FFAs with alcohol produces water that inhibits the transesterification of the glycerides.

In food frying, vegetable oils are used at very high temperatures. This process causes various chemical reactions such as hydrolysis, polymerization, and oxidation. Therefore, the physical and chemical properties of the oil change during frying. A great deal of research has been conducted to characterize these physical and chemical changes [56-59]. The percentage of FFAs has been found to increase due to the hydrolysis of triglycerides in the presence of food moisture and oxidation. As an example, the FFA level of fresh soybean oil changed from 0.04% to 1.51% after 70 hours of frying at 190°C [58]. Increases in viscosity were also reported due to polymerization, which resulted in the formation of higher molecular weight compounds. Other observations were that the acid value, specific gravity, and saponification value of the frying oil increased, but the iodine value decreased. The peroxide value increased to a maximum and than started to decrease. The cetane number of a used frying oil methyl ester was given as 49 [25].

In the transesterification of vegetable oil with alkaline catalysts, other researchers [60, 44] have emphasized that the vegetable oil and alcohol should not contain water and free fatty acids (FFA) since they slow the reaction. Romano [60] investigated the effect of water in soybean oil on transesterification with ethanol and 2% sodium hydroxide catalyst. When the water amount was changed from 0.15% to 0.66% in the reaction, the glycerine yields decreased from 95.4% to 73.2%.

Feuge et al. [61] studied the kinetics of catalyzed and uncatalyzed reactions in ester preparation using mixed fatty acids from peanut oil. They investigated the effects of temperature, pressure, and catalyst on the transesterification for an 8-hour reaction time. The reaction mixture contained FFAs as high as 90.3%. After a series of runs at 20 mm. Hg pressure and varying temperatures (166°C to 241°C) for uncatalyzed reactions, they noted that the FFA concentration in the mixture rapidly decreased as the reaction temperature was increased. They tested several catalysts at 200°C and 20 mm. Hg pressure and found zinc chloride ($ZnCl_2$) and stannous chloride ($SnCl_2 \cdot 2H_2O$) to be more effective than the others. They used 0.0008 moles of catalyst per 100 g of fatty acids in each case, and they tested the catalysts at various temperatures, 175°C to 250°C for zinc chloride and 150°C to 225°C for stannous chloride. They found that, especially at high temperatures, the catalyzed reaction followed an entirely different course from that of the uncatalyzed reaction and the concentration of FFA sharply decreased in 2 hours. When they extended their study to determine the effect of pressure over a range of pressure from 5-mm to 80-mm Hg, with 0.0008 mole (per 100 g of fatty acids) stannous chloride catalyst, the reaction rate displayed little influence. To investigate the effect of catalyst concentration, 0.0004 and 0.0016 moles zinc chloride were used. A decrease in the reaction rate was found when the catalyst concentration was decreased.

Freedman and co-workers [44] compared the transesterification of crude and refined cottonseed, peanut, soybean, and sunflower oils. They investigated the effects of acid value on the methyl ester yield with a 6:1 molar ratio. They noted that the free fatty acid level is higher in crude vegetable oils than in refined oils. The ester conversions decreased from 95% to 67%, 98% to 83%, 93% to 84%, 97% to 81%, for peanut, soybean, cottonseed, and sunflower oil, respectively, when crude oils were used. In that research, it was stressed that the yields of ester were reduced significantly when the acid value was higher than 1 mg KOH/g.

Keim et al. [62] studied esterification of fats and fatty oils containing over 50% free fatty acids. In this patent, unbleached palm oil containing 50.8% of free fatty acids was used.

After preparing a solution of methanol (77% of the weight of the oil) containing sulfuric acid (0.75% of the weight of the oil), it was added to the oil and stirred and heated at 69°C for an hour and the solution was neutralized with sodium hydroxide to a phenolphthalein end point. Then, a solution with 1.25% sodium methoxide was added and stirred for 1 hour at about 50°C. Then the product was acidified with 10% sulfuric acid and washed with water until neutral. The product was dried over anhydrous sodium sulfate, and filtered. Finally, the product was distilled under vacuum at a pressure of 4-mm Hg. The yield obtained was 97.0% and the acid value of the distillate was equivalent to about 5% as palmitic acid, which is still quite high for biodiesel to be used as an engine fuel.

Stern et al. [63] patented a three step transesterification process. The first step was an acid transesterification step in the presence of a branched monoalcohol of 1 to 5 carbon atoms containing 1 to 60% by weight of water. The second step was to reduce the acidity (FFA level) of the ester produced in the first step to about 2% using dry alcohol with a trace of acid catalyst. And the third step was base catalyst transesterification. They transesterified 500 g of palm oil containing 5.2% FFA as palmitic acid with 132 g of ethanol of 7% water content (because using absolute alcohol is more expensive) and 5 g of sulfonic acid (1% based on the oil weight) at 130°C for 2 hours. After cooling, the ester was separated from the glycerin. In the first step, the ester had a purity of 89%. In the second step, after evaporating the alcohol under vacuum, absolute ethanol with a trace of sulfonic acid was added to decrease the acidity of the ester fraction from 3.1 to 0.65%. In the third step, sodium hydroxide was added as a base catalyst, and the reaction was continued at 90°C for 0.5 hours. After washing 3 times with water and drying, the ester conversion was 98.7%. When they used methanol instead of ethanol in step 2, the FFA of the ester fraction decreased to 0.97%

and the conversion increased to 99.0%.

Jeromin et al. [64] developed a process for reducing the free fatty acid level of fats and oils below about 1 mg KOH/g. They used 50% to 150% excess methanol and about 0.1 to 0.2% by weight of sulfonic acid (the amounts depend on the free fatty acid content of oil), at a temperature from 55°C to 65°C. The reaction time varied from 10 to 60 minutes. They esterified coconut oil having an acid value of 10 mg KOH/g (which was the highest acid value among their examples) at 64°C. After the mixture was heated to about 120°C to evaporate the alcohol and water, the acid number was reduced to 0.55 mg KOH/g and the water content of the oil was 0.08% by weight.

Wimmer [65] received a patent for converting rapeseed oil with an acid value of 30 mg KOH/g (about 15% FFAs) to methyl esters. In this work, 5.2 g of potassium hydroxide were dissolved in 23 g of methanol and 20 g of the solution were introduced to 100 g of rapeseed oil and stirred for 15 minutes. After 1 hour of settling, glycerin and soap were separated, and the remaining 8.2 g of methanol solution was added and stirred again for 15 minutes. After an additional 1 hour of settling, the heavier phase was drained again and 3 ml of water were added and stirred for 10 minutes. The mixture was settled for another 2 hours, and the methyl ester was separated. The ester contained 1.6% residual fatty acids and 0.008% potassium.

Some researchers have focused specifically on transesterification of waste vegetable oils and their use in diesel engines. Mittelbach et al. [25] prepared methyl esters from used frying oil and compared their fuel properties to Austrian standards valid for rapeseed oil methyl ester. The content of the free fatty acids of the oils was between 0.26 to 2.12%. After filtration at 40°C to remove solid particles, the oil was transesterified using alkaline catalysis.

They noted that all specification values could be meet by the used vegetable oil esters except the cold filter plugging point, which in most cases was above −8°C.

Isigigur et al. [66] prepared 0, 10, and 20% blends (by volume) of methyl ester of used frying oil with No. 2 diesel fuel to compare their fuel properties. They found that the heating value and cetane number were a little lower than for No. 2 diesel fuel. The fuel properties of the 10 and 20% blends of the ester with diesel fuel were within the range of those for pure No. 2 diesel fuel.

Nye et al. [43] investigated the esters of used frying oil to determine their effects on engine performance and emissions. The esters of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-ethoxyethanol were prepared using sulfuric acid and potassium hydroxide as acid and base catalysts, respectively. They found that all the acid-catalyzed fuels had low viscosities, but all base-catalyzed fuels had higher viscosities, except for the methanol-based fuel, which was the least viscous of all fuels. The authors noted that the viscosity measurements of the esters correlated with the percentage of ester yield.

Mittelbach and Tritthart [67] prepared methyl esters from used frying oil. A solution of potassium hydroxide in methanol was added to used frying oil while stirring. It was allowed to settle for 5 hours to separate the glycerin and methyl ester. The ester was washed several times with warm water until the pH of the aqueous layer was neutral. After separating the aqueous layer and the ester, the ester was dried with anhydrous sodium sulfate and filtered.

Peterson et al. [68] produced biodiesel from waste hydrogenated soybean oil using 70% excess of the stoichiometric amount of ethanol. The total free fatty acids in the oil were neutralized with the addition of alkaline catalyst. Based on the oil weight, 1.3% of KOH was used plus the amount needed to neutralize the free fatty acids. Then the catalyst/alcohol mixture was pumped into the oil and the mixture stirred vigorously at 49°C for 2 hours. Ester and glycerin were separated after several hours of settling. Complete settling took as long as 20 hours. After settling was complete, wash water was added at the rate of 5.5% by volume of the oil and then stirred for 5 minutes and the glycerin was allowed to settle again. After settling was complete, the glycerin was drained and the ester layer remained. The ester was washed with the water containing 1 gram of tannic acid per liter of water. The water amount was 28% by volume of the oil. At the end, the ester was found to be 92.26% esterified and contained 0.3% free glycerin and 0.99% total glycerin.

Table 2.2 summarizes the effect of molar ratio, catalyst, catalyst amount, alcohol type, and temperature, on the ester conversion in transesterification processes of high FFA vegetable oils.

2.4. Pilot Plant Scale Transesterification

Some researchers have prepared larger amounts of biodiesel to investigate the effect on diesel engine performance and exhaust emissions. It is useful to review these studies because the preparation of large quantities of fuel can involve special problems and different techniques than preparation of small quantities. This is of particular interest since one of the tasks of this study is to implement the transesterification process in a pilot plant.

Hawkins and Fuls [69] used a 2200-liter reactor tank to prepare ethyl esters. In their research, after dissolving 7.5 kg of sodium hydroxide in 500 liters of ethanol, 1000 liters of degummed sunflower oil were added to the solution. The transesterification reaction continued overnight at room temperature (25°C). The catalyst was neutralized with 12 liters

Table 2.2: Summary of the transesterification processes of FFA and water content vegetable oils

Type of Oil and Alcohol (Molar Ratio)	*Amount of FFA (%)*	*Amount of Water (%)*	*Catalyst (%)*	*Temp. (°C)*	*Reaction Time*	*Conversion (%)*	*Ref. No.*
Coconut oil & ethanol (30% ethanol, as wt.)	Not Stated	0.15	Sodium Hydroxide (2.0)	Room	Not Stated	95.4	60
Coconut oil & ethanol (30% ethanol, as wt.)	Not Stated	0.36	Sodium Hydroxide (2.0)	Room	Not Stated	92.8	60
Coconut oil & ethanol (30% ethanol, as wt.)	Not Stated	0.66	Sodium Hydroxide (2.0)	Room	Not Stated	73.2	60
Used frying oil Methanol (1:3.6)	1.5	Not Stated	Potassium Hydroxide (0.4)	50	24 Hour	73.8	43
Used frying oil Methanol (1:3.6)	1.5	Not Stated	Sulfuric Acid (0.1)	~65	40 Hour	52.7	43
Used frying oil Ethanol (1:3.6)	1.5	Not Stated	Potassium Hydroxide (0.4)	50	24 Hour	46.1	43
Used frying oil Ethanol (1:3.6)	1.5	Not Stated	Sulfuric Acid (0.1)	~73	40 Hour	72.0	43
Used frying oil 1-propanol (1:3.5)	1.5	Not Stated	Potassium Hydroxide (0.4)	50	24 Hour	31.9	43
Used frying oil 1-propanol (1:3.5)	1.5	Not Stated	Sulfuric Acid (0.1)	~90	40 Hour	53.9	43
Used frying oil 2-propanol (1:3.5)	1.5	Not Stated	Potassium Hydroxide (0.4)	50	24 Hour	2.2	43
Used frying oil 2-propanol (1:3.5)	1.5	Not Stated	Sulfuric Acid (0.1)	~80	40 Hour	48.3	43
Used frying oil 1-butanol (1:3.6)	1.5	Not Stated	Potassium Hydroxide (0.4)	50	24 Hour	47.7	43
Used frying oil 1-butanol (1:3.6)	1.5	Not Stated	Sulfuric Acid (0.1)	~105	40 Hour	81.3	43
Used frying oil 2-exhoxyethanol (1:3.5)	1.5	Not Stated	Potassium Hydroxide (0.4)	50	24 Hour	29.4	43
Used frying oil 2-exhoxyethanol (1:3.5)	1.5	Not Stated	Sulfuric Acid (0.1)	~125	40 Hour	47.5	43

Table 2.2: continued

Type of Oil and Alcohol (Molar Ratio)	*Amount of FFA (%)*	*Amount of Water (%)*	*Catalyst (%)*	*Temp. (°C)*	*Reaction Time*	*Conversion (%)*	*Ref. No.*
Refined Peanut oil Methanol (1:6)	Acid Value 0.08 mg KOH/g	Not Stated	Sodium Methoxide	Not Stated	Not Stated	95.0	44
Crude Peanut oil Methanol (1:6)	Acid Value 6.66 mg KOH/g	Not Stated	Sodium Methoxide	Not Stated	Not Stated	67.0	44
Refined Soybean oil Methanol (1:6)	Acid Value 0.12 mg KOH/g	Not Stated	Sodium Methoxide	Not Stated	Not Stated	98.0	44
Crude Soybean oil Methanol (1:6)	Acid Value 1.67 mg KOH/g	Not Stated	Sodium Methoxide	Not Stated	Not Stated	83.0	44
Refined Cottonseed oil Methanol (1:6)	Acid Value 0.06 mg KOH/g	Not Stated	Sodium Methoxide	Not Stated	Not Stated	93.0	44
Crude Cottonseed oil Methanol (1:6)	Acid Value 0.28 mg KOH/g	Not Stated	Sodium Methoxide	Not Stated	Not Stated	84.0	44
Refined Sunflower oil Methanol (1:6)	Acid Value 0.08 mg KOH/g	Not Stated	Sodium Methoxide	Not Stated	Not Stated	97.0	44
Crude Sunflower oil Methanol (1:6)	Acid Value 1.64 mg KOH/g	Not Stated	Sodium Methoxide	Not Stated	Not Stated	81.0	44
Palm oil & methanol (77% methanol as the weight of the oil) (2 Step Reaction)	50.8	Not Stated	Sulfuric Acid (0.75%)	69 & 50	1 + 1 Hours	97.0 (Still Contains 5% Palmitic Acid)	62
Palm oil & ethanol (1:4.5) (3 Step Reaction)	5.2	7	Sulfonic Acid (1.0%)	130 & 90	2 + 0.5 Hours	98.7	63
Palm oil & ethanol + methanol (in Step2) (1:4.5) (3 Step Reaction)	5.2	7	Sulfonic Acid (1.0%)	130 & 60	2 + 0.5 Hours	99.0	63

of ortho-phosphoric acid to get a low pH, which was done to prevent soap formation during water washing. After 2 more hours of agitation, the mixture was allowed to sit for 6 hours to facilitate the settling of glycerin and salts. The ethyl ester was washed at 80°C with an amount of water equal to 35% of the ester volume until a pH of around 6.5 was reached in the wash water.

Hassett and Hasan [70] prepared methyl esters from sunflower oil in 9-liter batches. They mixed 9 liters of sunflower oil with 1456 grams of methanol to which 8.4 grams of metallic sodium had been added. The mixture was stirred for 2 hours at 62°C - 65°C. After the glycerin and ester separation, the methyl ester was washed with warm water to remove the suspended glycerin, unreacted methanol, and catalyst. The washed ester was dried with anhydrous sodium sulfate and then used as fuel grade sunflower oil methyl ester. After transesterification the FFA level was reduced from 1.46 to 0.2%.

Nye and Southwell [71] investigated the pilot plant transesterification of crude rapeseed oil. A twenty-five liter batch reaction was conducted in an enclosed stainless steel cylindrical drum stirred by a 40-cm diameter propeller driven by a 1/3-hp electric motor. After dissolving 1% NaOH in 6 molar equivalents of dry methanol or ethanol, the crude rapeseed oil was added to the solution. The mixture was stirred with splashing for 1 hour at 24°C. After extracting the ester, it was washed three times with a volume of water equal to half of the volume of oil, then dried over anhydrous $CaCl_2$ and filtered to remove fine particles. The ester conversion was 92% and 95% for methyl and ethyl ester, respectively.

Fuls et al. [36] used 1400 liters of sunflower oil to prepare ethyl esters. After dissolving 10.5 kg of sodium hydroxide in 600 liters of ethanol, the oil was added to the solution and reacted at 30°C for 4 hours. The mixture was allowed to settle so that the glycerin could be drained off before heating was used to evaporate the excess alcohol. The hot ester was then gently washed 4 times with water (10% of total volume) at about 25°C, draining off the water after each wash. After cooling the ester to room temperature, it was centrifuged to get high quality ester and the specific gravity of the ester was 0.879 at 20°C.

Peterson et al. [72] described a batch type transesterification process for winter rape oil. They designed a transesterification plant with a 200-gallon capacity, although, typically, 160-gallon batches were produced. The components of the plant were: a 290 gallon cone bottom, cross-linked polyethylene tank, a centrifugal pump (20-25 gallon per minute capacity), a ¼ hp mixer with 3.4:1 gear reduction (1725 rpm motor speed and 514 rpm rotor speed), and a 1 hp gear pump was used to transfer the raw vegetable oil and the finished ester to the storage tank. After methanol and KOH were mixed in a smaller (50-gallon) tank, the solution was transferred into the large tank. All of the reaction, settling, washing, and separating took place in this one large tank. After 4 to 6 hours of reaction time, the mixture was allowed to settle for 12 hours or more to allow the glycerin to settle to the bottom. Then the glycerin was drained from the bottom. In the washing process, water was sprinkled into the tank from a common lawn sprinkler at the approximate rate of 100 gal/hr. As the water droplets traveled through the ester they removed the KOH, methanol, and other impurities. After 20 to 30 hours of washing, the mixture was allowed to sit for 3 to 4 days. The water settled to the bottom and was visible as a white layer. At this time, the clean methyl ester was pumped into a storage tank. The ester conversion obtained was 98% and above.

Mittelbach and Tritthart [67] prepared methyl esters of used frying oil to be used for engine tests after collecting about 200 kg of used frying oil from different households and restaurants. For the transesterification reaction, a 50-liter glass vessel equipped with a mechanical stirrer was used. A solution of 450 g of potassium hydroxide in 8 liters of methanol was added to 40 kg of vegetable oil while stirring. After a 20-minute reaction period, the mixture slowly became clear and less viscous. It was allowed to settle for 5 hours to separate the glycerin and methyl ester. The ester was washed several times with 10 liters of water at 40°C until the pH of the aqueous layer was neutral. After separating the aqueous layer and the ester, the ester was dried with 4 kg of anhydrous sodium sulfate and filtered.

Peterson et al. [68] produced 1000 liters of biodiesel from ethanol and waste hydrogenated soybean oil. They used 70% excess of the stoichiometric amount of ethanol. The total free fatty acids were determined and neutralized with the calculated addition of alkali catalyst. Based on the amount of input oil by weight, 1.3% of KOH was used plus the amount needed to neutralize the free fatty acids. The waste hydrogenated soybean oil was heated to 49°C. The oil was transferred into the biodiesel reactor and then the catalyst/alcohol mixture was pumped into the oil and the final mixture stirred vigorously for 2 hours. The ester and glycerin were separated after several hours of settling. Complete settling took as long as 20 hours. After settling was complete, wash water was added at the rate of 5.5% by volume of the oil and then stirred for 5 minutes and the glycerin was allowed to settle again. After settling was complete, the glycerin was drained and the ester layer remained. They washed the ester in a two step process. A wash water solution containing 1 gram of tannic acid per liter of water was added at the rate of 28% by volume of the oil and gently agitated. Air was carefully introduced into the aqueous layer while simultaneously stirring very gently. This process was continued until the ester layer became clear. The authors did not state whether there was any intended chemical function of the air introduced to the ester. It was apparently included to provide additional agitation. After settling, the aqueous solution was drained and water alone was added at 28% by volume of oil for the final washing. In that study, the final product ester was found to be 92.26% esterified and contained 0.3% free glycerin and 0.99% total glycerin. This fuel exceeded the standards in the provisional ASTM specification of 0.02% free glycerin and 0.24% total glycerin. The concentration of monoglycerides were 1.49%, the diglycerides 4.23% and the triglycerides were 0.99%. The remaining amounts of alcohol and catalyst were 0.012% and 32 microgram/gram, respectively.

Table 2.3 summarizes the different studies of pilot plant scale transesterification of vegetable oils.

2.5. Waste Restaurant Grease and Animal Fat in the United States and Iowa

Inedible oil from spoiled soybeans, waste oils and greases from restaurants and food service facilities, beef, pork, and chicken fat from packing plants are all possible sources of lower cost feedstocks for biodiesel. Waste oils and fats are currently collected from large food processing and service facilities where they are rendered and used almost exclusively in animal feed.

The US Department of Energy's National Renewable Energy Laboratory (NREL) sponsored a study on urban waste grease resources in 30 randomly selected metropolitan areas in the United States [73]. This study showed that an average of 9 pounds/year/person of yellow grease and 13 pounds/year/person of trap grease were produced in 1998. ***Yellow grease*** is an agricultural commodity that is produced from rendered animal fats and restaurant waste oil and grease. It is required to have a free fatty acid (FFA) level of less than 15%. If the FFA level exceeds 15%, it may be sold at a discount as brown grease, or blended

Table 2.3: Summary of the large scale transesterification processes

Amount and Oil Type	***Amount and Alcohol Type***	***Amount and Catalyst Type***	***Reaction***		***Washing Time***	***Amount of Wash Water***	***Wash Water Temp.***	***(%) Ester Conversion***	***Ref. No.***
			Temp.	***Time***					
1000 Liters Sunflower Oil	500 Liters Ethanol	7.5 kg Sodium Hydroxide	25°C	Overnight	Until pH of around 6.5 in Washing Water	35% of the Ester Volume	80°C	Not Stated	69
9 Liters Sunflower Oil	1456 grams Methanol	8.4 g Sodium	~65°C	2 Hours	Not Stated	Not Stated	Warm	Not Stated	70
25 Liters Rapeseed Oil	6:1 Molar Ratio Methanol	1wt% Sodium Hydroxide (Based on the Oil)	24°C	1 Hour	3 Times	½ of the Ester Volume	Not Stated	92	71
25 Liters Rapeseed Oil	6:1 Molar Ratio Ethanol	1wt% Sodium Hydroxide (Based on the Oil)	24°C	1 Hour	3 Times	½ of the Ester Volume	Not Stated	95	71
1400 Liters Sunflower Oil	600 Liters Ethanol	10.5 kg Sodium Hydroxide	30°C	4 Hours	4 Times	10% of the Ester Volume	25°C	Not Stated	36
151 Liters Winter Rapeseed Oil	34 Liters Methanol	1.46 kg Potassium Hydroxide	Room Temp.	4-6 Hours	Until the Level raises 8 to 10 in. (in the Tank)	100 gal/h (Sprinkled in the Tank)	Not Stated	≥98	72
605 Liters Winter Rapeseed Oil	136 Liters Methanol	5.84 kg Potassium Hydroxide							
756 Liters Winter Rapeseed Oil	170 Liters Methanol	7.30 kg Potassium Hydroxide							
40 kg Used Frying Oil	8 Liters Methanol	450 g Potassium Hydroxide	Room Temp.	20 Minutes	Several Times	10 Liters	40°C	Not Stated	67
Waste Hydrogenated Soybean Oil (at 49 °C)	70% Excess Ethanol	neutralization amount + 1.3% Potassium Hydroxide	Room Temp.	2 Hours	2 Times	28% of the Ester Volume	Not Stated	92.26	68

with low FFA material to meet the yellow grease specifications. The price of yellow grease varies widely from $0.09 - $0.20/lb [74]. Brown grease is usually discounted $0.01 - $0.03 below this [75]. Trap grease is material that is collected in special traps in restaurants to prevent the grease from entering the sanitary sewer system where it could cause blockages. Trap grease is often cited as a potential feedstock for biodiesel because it currently has very low value. Many rendering plants will not process trap grease because it is usually contaminated with cleaning agents. These cleaning agents may not themselves be hazardous but they make detection of harmful substances more difficult.

Table 2.4 shows quantitative data for yellow grease and trap grease from 30 metropolitan areas in the United States. Although the cities ranged in size from 83,831 (Bismarck, ND) to 3,923,574 (Washington, DC), no Iowa cities were included. These data show that the cities had an average of 1.4 restaurants per 1000 population and that 8.87 lbs. of yellow grease were produced per person per year. Although the range of the data were fairly wide, the NREL study also concluded that the volume of the waste restaurant grease produced correlated to general population as well as to the number of restaurants.

The Waste Management Assistance Division of the Iowa Department of Natural Resources published an executive summary about rendering operations in the State of Iowa in December 1996 [76]. This report was the result of a rendering facility survey. Table 2.5 shows the amount of material processed by rendering plants in Iowa. The estimate of 13,799 tons/year of used restaurant grease is actually quite close to the estimate developed from the NREL study. If each of Iowa's 2.8 million population generates 8.87 pounds/year of restaurant grease, this equals 11,350 tons/year.

In Iowa, the majority of the yellow grease produced by some rendering plants

Table 2.4: Urban waste grease resources in 30 metropolitan areas [73]

No.	Metro Area	State	Population	*Urban Waste Grease Resources (Pounds/Year)*				*Urban Waste Grease Resources (Pounds/Year/Person)*			
				No. of Restaurants	*Yellow Grease*	*Trap Grease*	*Total Grease*	*Restaurant /1000 P*	*Yellow Grease*	*Trap Grease*	*Total Grease*
1	Sacramento	CA	1,481,102	2,200	4,500,000	16,600,000	21,100,000	1.49	3.04	11.21	14.25
2	Olympia	WA	161,238	240	1,080,000	1,200,000	2,280,000	1.49	6.70	7.44	14.14
3	Provo	UT	263,590	400	4,380,000	7,000,000	11,380,000	1.52	16.62	26.56	43.17
4	Denver	CO	1,848,319	2,670	17,000,000	15,900,000	32,900,000	1.44	9.20	8.60	17.80
5	Lincoln	NE	213,641	350	4,500,000	2,600,000	21,600,000*	1.64	21.06	12.17	101.10**
6	Bismarck	ND	83,831	133	430,000	400,000	830,000	1.59	5.13	4.77	9.90
7	Bloomington	IL	129,180	200	500,000	2,300,000	2,800,000	1.55	3.87	17.80	21.68
8	Battle Creek	MI	135,982	211	1,500,000	1,500,000	3,000,000	1.55	11.03	11.03	22.06
9	Mansfield	OH	126,137	244	650,000	190,000	840,000	1.93	5.15	1.51	6.66
10	Elmira	NY	95,195	140	950,000	1,500,000	2,450,000	1.47	9.98	15.76	25.74
11	Boston	MA	1,950,855	3,000	10,400,000	33,600,000	44,000,000	1.54	5.33	17.22	22.55
12	Harrisburg	PA	587,986	900	6,000,000	10,800,000	16,800,000	1.53	10.20	18.37	28.57
13	Altoona	PA	130,542	143	1,300,000	1,000,000	2,300,000	1.10	9.96	7.66	17.62
14	Hagerstown	MD	121,393	170	1,200,000	1,000,000	2,200,000	1.40	9.89	8.24	18.12
15	Washington	DC	3,923,574	5,000	39,000,000	50,000,000	89,000,000	1.27	9.94	12.74	22.68
16	Richmond	VA	865,640	1,480	8,700,000	17,300,000	26,000,000	1.71	10.05	19.99	30.04
17	Danville	VA	108,711	157	1,100,000	1,900,000	3,000,000	1.44	10.12	17.48	27.60
18	Fayetteville	NC	274,566	384	2,700,000	2,100,000	4,800,000	1.40	9.83	7.65	17.48
19	Florence	SC	114,344	185	1,100,000	900,000	2,000,000	1.62	9.62	7.87	17.49
20	Greenville	SC	640,861	1,017	6,400,000	4,600,000	11,000,000	1.59	9.99	7.18	17.16
21	Lexington	KY	348,428	562	3,500,000	3,600,000	7,100,000	1.61	10.05	10.33	20.38
22	Memphis	TN	981,747	1,128	9,800,000	18,500,000	28,300,000	1.15	9.98	18.84	28.83
23	Decatur	AL	131,556	245	1,300,000	2,400,000	3,700,000	1.86	9.88	18.24	28.12
24	Macon	GA	281,103	348	2,800,000	5,900,000	8,700,000	1.24	9.96	20.99	30.95

Table 2.4: continued

No.	*Metro Area*	*State*	*Population*	*Urban Waste Grease Resources (Pounds/Year)*				*Urban Waste Grease Resources (Pounds/Year/Person)*			
				No. of Restaurants	*Yellow Grease*	*Trap Grease*	*Total Grease*	*Restaurant /1000 P*	*Yellow Grease*	*Trap Grease*	*Total Grease*
25	Lakeland	FL	405,382	445	4,100,000	4,600,000	8,700,000	1.10	10.11	11.35	21.46
26	Bradenton	FL	211,707	360	2,100,000	3,000,000	5,100,000	1.70	9.92	14.17	24.09
27	Baton Rouge	LA	528,264	657	5,300,000	5,800,000	11,100,000	1.24	10.03	10.98	21.01
28	Shreveport	LA	334,341	442	3,300,000	4,700,000	8,000,000	1.32	9.87	14.06	23.93
29	Beaumont	TX	361,226	383	3,600,000	3,900,000	7,500,000	1.06	9.97	10.80	20.76
30	Bryan	TX	121,862	198	1,200,000	2,000,000	3,200,000	1.62	9.85	16.41	26.26
							Weighted Average	*1.41*	*8.87*	*13.37*	*23.09*

*Lincoln total includes 14,500,000 pounds/year of food plant waste grease.

**Lincoln total includes 67.87 pounds/year/person of food plant waste grease.

originates from animal carcasses with more than 10 times the volume of used restaurant grease. In states with less livestock production and numerous large urban centers, the ratio may be reversed. Table 2.6 shows the volume of rendered product sold in Iowa. The animal/livestock feed is mostly meat and bone meal which is the solid by-product of the rendering of animal carcasses. Although the DNR report did not identify it as such, the tallow shown is probably edible tallow that is produced by rendering by-product fat in meat packing plants. The grease shown is yellow and brown grease and would be the candidate feedstock for biodiesel. While edible tallow could be used for biodiesel, its value as a food ingredient makes it more expensive than grease.

Since one pound of most fats and oils can be converted to a pound of biodiesel, if all of the 23,586 tons/year of grease were converted to biodiesel, it would produce about 47 million pounds of biodiesel which would displace about 6 million gallons of diesel fuel.

2.6. Chemical Analysis of Unprocessed Restaurant Grease and Animal Fat

Very few data are available in the literature for the actual composition of the feedstocks to rendering plants. As part of this study samples of rendering plant feedstocks and final products were collected and analyzed to define the range of properties that should be expected for a pilot plant operating on high FFA feedstock. Table 2.7 shows the detailed chemical analysis of samples of rendering plant feedstocks and final products collected from Simonsen Rendering Co. in Quimby, Iowa. Simonsen receives both restaurant grease and animal carcasses but processes these two streams separately before blending them together as a final product. The samples identified as SIM-01, SIM-05, SIM-09, SIM-10, and SIM-11 are restaurant grease as received by the rendering plant. The moisture level of these samples

Table 2.5: The amount of rendered waste in Iowa in 1996 [76]

Waste Type	*Amount (tons/year)*	*Respondent %*
Animal Carcasses	157,480	71
Offal	179,398	71
Fat/Bone	143,624	57
Fish Waste	305	29
Food Waste	15	14
Used Restaurant Grease	13,799	57
Blood	43,206	29
Feathers	14,651	14
Total Material Rendered	*552,478*	

Table 2.6: Rendering plant product [76]

Bulk	*Responding Number*	*Total (tons)*	*Price Range (per pound)*	*Average Price*
Animal/Livestock Feed	5 (71%)	132,046	\$0.09 - \$0.14	\$0.12
Tallow	4 (57%)	79,120	\$0.10 - \$0.20	\$0.17
Grease	6 (86%)	23,586	\$0.07 - \$0.20	\$0.16
Blood	1 (14%)	5,823	\$0.20	\$0.20
Hydrolyzed Feather Meal	1 (14%)	3,582	\$0.125	\$0.125

varies widely with one being as high as 18%. The free fatty acid levels also varied from 0.7% to 41.8%. These data indicate that a process to convert waste restaurant grease to biodiesel must be very robust, and capable of tolerating a wide range of feedstock properties.

The other data shown in Table 2.7 show the properties for a variety of finished greases. These products generally have less than 2% MIU (moisture, insolubles, and unsaponifiables). The FFA levels of these finished greases varies from about 8.8 to 25.5.

Figure 2.3 from another source in the rendering industry shows the variation in FFA level of animal fat over a typical year. From May to October, the FFA level exceeds 15% so it must be blended with fat from other sources to meet the yellow grease specification. These high FFA levels are associated with the rapid degradation of animal carcasses during hot weather.

Table 2.7: Chemical Analysis Results of Reastaurant Grease and Animal Fat Samples

TEST / SAMPLE	Refined Soybean Oil 1	Refined Soybean Oil 2	FG-1/A	SIM-01	SIM-02	SIM-03	SIM-04	SIM-05	SIM-07	SIM-08	SIM-09	SIM-10	SIM-11	SIM-24
M I U (%)	0.44	0.41	1.61	24.11	0.74	2.85	3.54	0.98	6.42	58.14	1.71	1.06	1.97	2.37
Moisture & Volatiles by Hot Plate	0.01	<0.10	0.20	18.06	0.31	0.11	3.11	0.35	0.26	55.38	1.26	0.65	1.42	0.35
Insoluble Impurities (%)	<0.10	<0.10	0.36	1.22	<0.10	0.11	0.09	0.11	3.83	2.51	0.03	0.03	0.08	1.03
Unsaponifiable Matter (%)	0.43	0.41	1.05	4.83	0.43	2.63	0.34	0.52	2.33	0.25	0.42	0.38	0.47	0.99
Peroxide Value (*meq/kg*)	66	7.3	0.4	0.8	4.0	<0.2	3.7	3.4	<0.2	0.6	4.6	3.1	1.7	1.0
F. F. A. (%)	0.02	0.01	8.8	41.8	9.7	25.7	2.6	1.1	25.5	14.8	0.7	1.3	0.7	10.5
FATTY ACID PROFILE (%)														
C08:0 Octanoic (Caprylic)	<0.10	<0.10	<0.10	0.21	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
C10:0 Decanoic (Capric)	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
C11:0 Undecanoic (Hendecanoic)	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
C12:0 Dodecanoic (Lauric)	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
C13:0 Tridecanoic	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
C14:0 Tetradecanoic (Myristic)	<0.10	<0.10	1.73	2.79	0.45	1.52	0.59	0.19	1.56	0.43	0.20	0.49	0.18	1.45
C14:1 Tetradecenoic (Myristoleic)	<0.10	<0.10	0.16	0.63	<0.10	0.15	0.11	<0.10	0.17	<0.10	<0.10	<0.10	<0.10	0.13
C15:0 Pentadecanoic	<0.10	<0.10	0.23	0.43	<0.10	0.15	<0.10	<0.10	0.17	<0.10	<0.10	<0.10	<0.10	0.18
C15:1 Pentadecenoic	<0.10	<0.10	<0.10	0.18	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
C16:0 Hexadecanoic (Palmitic)	10.29	10.40	21.75	25.92	12.84	22.39	13.44	11.49	22.46	12.74	10.92	13.67	10.91	20.51
C16:1 Hexadecenoic (Palmitoleic)	<0.10	<0.10	4.45	3.79	1.12	3.14	1.24	0.64	3.06	0.88	0.44	0.95	0.28	3.58
C16:2 Hexadecadienoic	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
C16:3 Hexadecatrienoic	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
C16:4 Hexadecatetraenoic	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
C17:0 Heptadecanoic (Margaric)	0.11	<0.10	0.56	1.09	0.22	0.53	0.28	0.13	0.57	0.24	0.14	0.22	0.14	0.49
C17:1 Heptadecenoic Margaroleic	<0.10	<0.10	0.44	0.71	0.15	0.39	0.19	<0.10	0.41	0.14	<0.10	0.16	<0.10	0.39
C18:0 Octadecanoic (Stearic)	4.28	4.51	12.05	16.49	7.18	12.81	7.59	5.69	13.33	8.22	5.05	7.45	6.61	11.43
C18:1 Octadecenoic (Oleic)	21.55	24.37	40.61	39.54	43.49	42.53	42.11	29.37	42.74	41.52	33.47	37.70	37.22	41.87
C18:2 Octadecadienoic (Linoleic)	53.68	51.90	11.03	4.40	29.47	12.07	29.33	44.77	10.89	30.86	42.64	33.48	38.33	13.98
C18:3 Octadecatrienoic (Linolenic)	8.16	6.52	1.38	0.57	2.66	0.81	2.86	5.38	0.67	2.96	4.90	3.58	4.22	1.41
C18:4 Octadecatetraenoic	<0.10	<0.10	0.32	0.25	0.30	0.10	0.27	<0.10	0.12	0.20	0.21	0.19	0.23	0.25
C20:0 Eicosanoic (Arachidic)	0.34	0.37	0.19	0.18	0.32	0.20	0.33	0.35	0.21	0.34	0.35	0.33	0.37	0.22
C20:1 Eicosenoic (Gadoleic)	0.19	0.28	1.13	0.66	0.57	1.01	0.53	0.39	1.04	0.46	0.45	0.46	0.45	1.06
C20:2 Eicosadienoic	<0.10	<0.10	0.49	<0.10	<0.10	0.50	<0.10	<0.10	0.44	<0.10	<0.10	<0.10	<0.10	0.41
C20:3 Eicosatrienoic	<0.10	<0.10	0.24	<0.10	<0.10	0.19	<0.10	<0.10	0.19	<0.10	<0.10	<0.10	<0.10	0.20
C20:4 Eicosatetraenoic (Arachidonic)	<0.10	<0.10	0.65	<0.10	<0.10	0.43	<0.10	<0.10	0.41	<0.10	<0.10	<0.10	<0.10	0.54
C20:5 Eicosapentaenoic	<0.10	<0.10	0.55	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.35
C21:5 Heneicosapentaenoic	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
C22:0 Docosanoic (Behenic)	0.37	0.39	<0.10	<0.10	0.33	<0.10	0.33	0.35	<0.10	0.34	0.37	0.30	0.36	<0.10
C22:1 Docosenoic (Erucic)	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10

Table 2.7: continued

TEST / SAMPLE	Refined Soybean Oil 1	Refined Soybean Oil 2	FG-1/A	SIM-01	SIM-02	SIM-03	SIM-04	SIM-05	SIM-07	SIM-08	SIM-09	SIM-10	SIM-11	SIM-24
C22:2 Docosadienoic	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
C22:3 Docosatrienoic	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
C22:4 Docosatetraenoic	<0.10	<0.10	0.19	<0.10	<0.10	0.19	<0.10	<0.10	0.18	<0.10	<0.10	<0.10	<0.10	0.17
C22:5 Docosapentaenoic	<0.10	<0.10	0.25	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.20
C22:6 Docosahexaenoic	<0.10	<0.10	0.21	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.16
C24:0 Tetracosanoic (Lignoceric)	0.12	0.13	<0.10	<0.10	<0.10	<0.10	0.10	0.11	<0.10	<0.10	0.12	<0.10	0.12	<0.10
C24:1 Tetracosenoic (Nervonic)	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Unknown Components (%)	0.91	1.13	1.39	2.16	0.90	0.89	0.70	1.14	1.38	0.67	0.74	1.02	0.58	1.02

The notations about the restaurant grease and animal fats are following.

SIM-01	Unprocessed restaurant grease. As delivered. Collected from the tops of 3 separate barrels. Water mostly at the bottoms of the barrel. Collected 9/28/1998.
SIM-02	Restaurant grease. Boiled and settled. This is the final product before mixing with animal fat. Collected 9/24/1998.
SIM-03	Animal fat. This was the final product for their animal fat but before it is mixed with any restaurant grease. Collected 9/23/1998.
SIM-04	Processed restaurant grease. Collected 12/29/1998.
SIM-05	Restaurant grease. Skimmed from top of barrel. Collected 2/21/1999.
SIM-07	Mixed fat from storage tank. This is the final product as sold. Collected 9/25/1998.
SIM-08	Restaurant grease, partially processed. This material had been through the first stage of processing, where the solids and free water are removed but it had not been cooked. Collected 10/1/1998.
SIM-09	Restaurant grease. Skimmed from top of barrel. Collected 12/24/1998.
SIM-10	Restaurant grease. Skimmed from top of barrel. Collected 2/22/1999.
SIM-11	Restaurant grease. Skimmed from top of barrel. Collected 2/20/1999.
SIM-24	Finished grease, with some restaurant grease. No collection date given.
FG-1A	5 gallon bucket of straight animal fat, approximately 10% FFA. Collected 2/24/1998.

Figures 2.4 and 2.5 are from the same source as Figure 2.3. They show that the fatty acid profile of the animal fat and its iodine value do not vary much during the year. The iodine value is a measure of the level of saturation of the fat.

2.7. Diesel Engine Emissions Fueled with Vegetable Oil Esters

Vegetable oil esters are receiving increasing attention as an alternative, non-toxic, biodegradable and renewable diesel fuel. Many studies have shown that the properties of biodiesel are very close to diesel fuel. Therefore, biodiesel fuel can be used for diesel engines with little or no modification. Biodiesel has a higher cetane number than diesel fuel, no aromatics, 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 diesel fuel. This section will review a portion of the studies in the literature on biodiesel performance, combustion, and emissions.

Schmidt and Van Gerpen [18] used a four cylinder, turbocharged, direct injection diesel engine to investigate biodiesel's emission reduction effect and the effect of blends of esters (20% and 50% blends in No. 2 diesel fuel) with diesel fuel on engine performance and emission. The engine was fueled with different esters (methyl soyate derived from soybean oil, methyl palmitate, methyl stearate, methyl oleate derived from a commercial grade of oleic acid, isopropyl palmitate, isopropyl stearate, methyl ester of safflower oil, and methyl ester of linseed oil) and blends of these esters at 20% and 50% in No. 2 diesel fuel.

Particulate emissions were significantly reduced when the engine was fueled with the blends of methyl palmitate. The 50% blend of methyl palmitate gave the largest particulate reduction of 30%. They reported that the HC emissions decreased as the percent ester

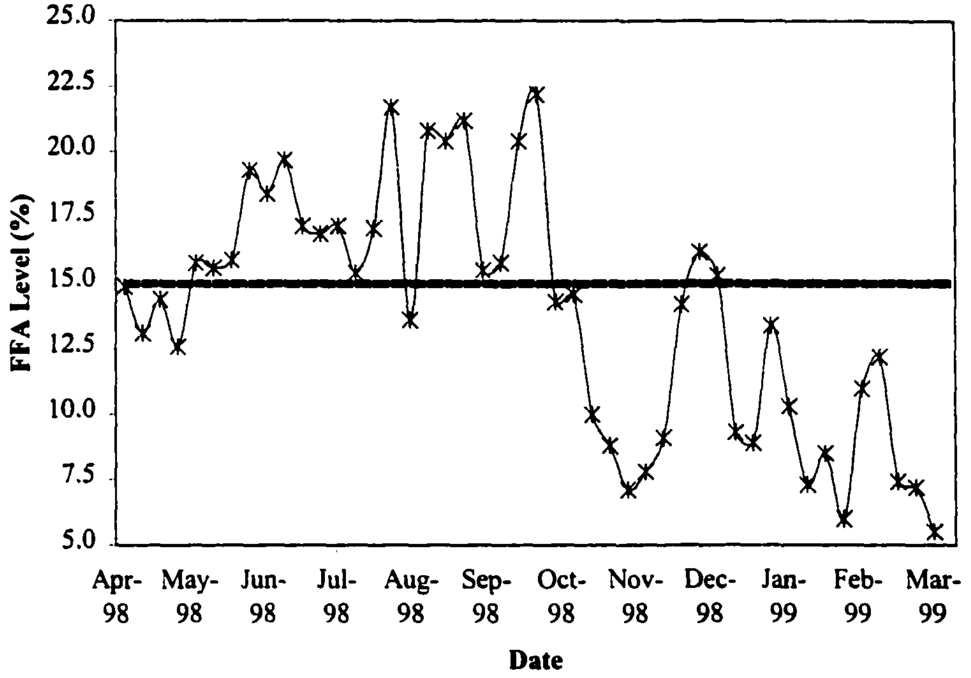


Figure 2.3: The change in the FFA level of the animal fat during a year

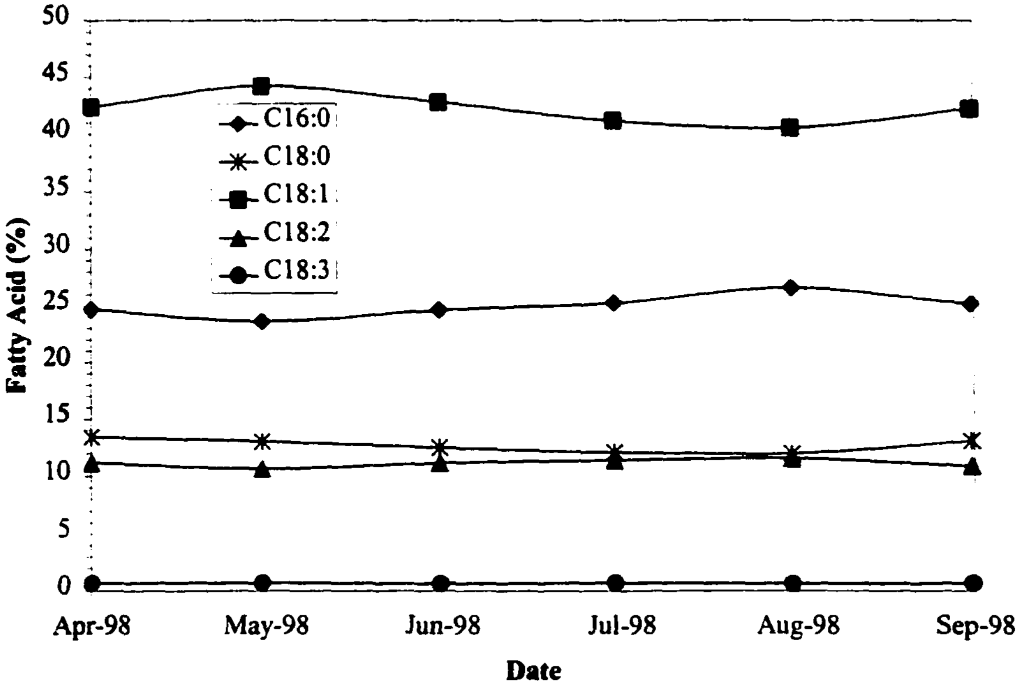


Figure 2.4: The change in the fatty acid profile of the animal fat

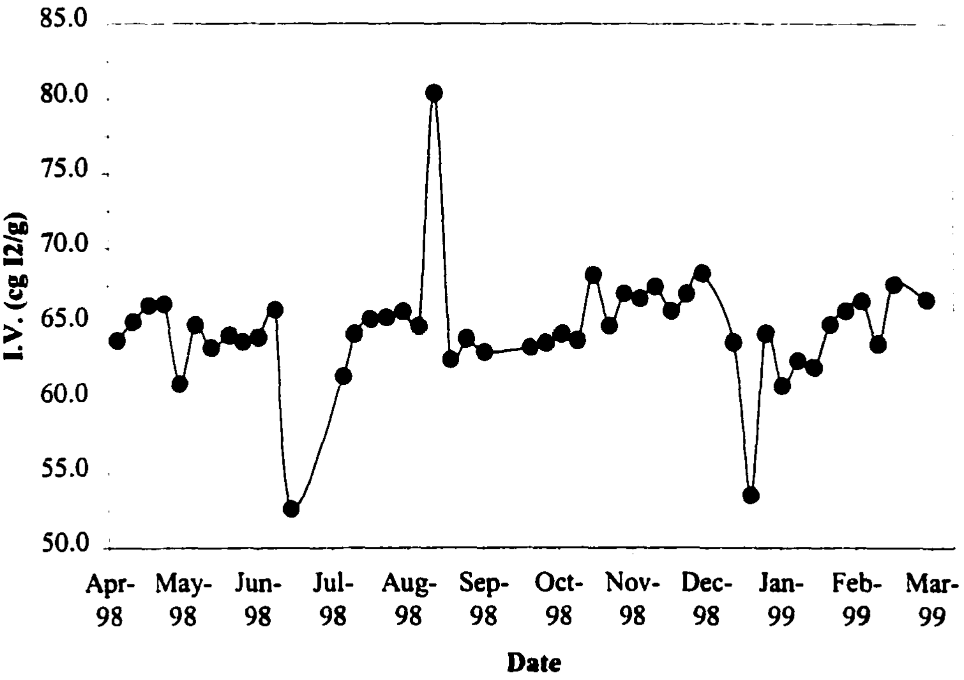


Figure 2.5: The change in the iodine value of the animal fat during a year

increased for all of the esters. The most significant reduction in HC emissions, about 30%, was reported for methyl stearate and methyl palmitate esters. The NO_x emissions did not change significantly for any of the esters. They noted that CO emissions reduction was not significant but that methyl stearate and methyl palmitate appeared to reduce CO the most when they were blended with diesel fuel. The BSFC of the esters increased as the amount of ester in the fuel increased, due to the lower energy content of the biodiesel fuels.

Scholl and Sorenson [3] investigated the combustion of soybean oil methyl ester in a direct injection diesel engine and compared it to that of diesel fuel. They found that the soybean oil methyl ester behaved comparably to diesel fuel in terms of performance and rate of heat release. They noted that NO_x emissions were strongly related to the cylinder pressure. They also tested the fuels using two different injection nozzle orifice diameters. Changing the injector orifice diameter had less effect on engine performance when using diesel fuel than with methyl ester fuel. A smaller orifice diameter gave higher cylinder pressure and maximum rate of pressure increase, higher NO_x emissions, and a larger amount of premixed burning for both fuels. The CO emissions from the soybean oil methyl ester were slightly lower than those from the diesel fuel. At optimum operating conditions, lower HC emissions and smoke number were found for the methyl ester. The HC emissions from the methyl ester were about one half of those from the diesel fuel. The Bosch smoke numbers for the soybean oil methyl ester were also lower than for the diesel fuel.

Alfuso et al. [77] fueled a direct injection, turbocharged diesel engine with the methyl ester of rapeseed oil to investigate its effect on exhaust emissions. They found that, at the same injection timing, the methyl ester caused an increase in NO_x emissions, a decrease in HC and CO emissions, as well as a strong reduction of smoke. The particulate matter produced by the methyl ester in transient cycles was higher than that obtained with diesel fuel. They reported that NOx, HC, and CO emissions of biodiesel may be reduced by the adoption of EGR in the presence of an exhaust oxidation catalyst.

Monyem [78] investigated the effect of biodiesel oxidation on engine performance and emissions. Monyem prepared oxidized biodiesel by bubbling pure O_2 into biodiesel at 60°C until the peroxide value of the biodiesel reached 340 meq O_2/kg. The engine performance of both the oxidized and unoxidized biodiesel were similar to that of No. 2 diesel fuel with nearly the same thermal efficiency but with higher fuel consumption reflecting the lower energy content of the biodiesel fuels. The CO and HC emissions and smoke number were found to be between 14% and 16% lower compared to unoxidized biodiesel. There was no statistically significant difference in the NO_x emissions for oxidized and unoxidized biodiesel.

Chang et al. [20] tested a four-cylinder turbocharged diesel engine fueled with blends of methyl and isopropyl esters of soybean oil in No. 2 diesel fuel to determine the engine's performance and emissions. They tested fuel blends which were 20, 50, and 70% soybean oil methyl ester and 20 and 50% soybean oil isopropyl ester. Their results showed that engine performance for all of the fuel blends was similar to No. 2 diesel fuel. They reported that all blends of methyl and isopropyl esters of soybean oil with No. 2 diesel fuel produced lower emissions of CO and unburned HC than the diesel fuel itself. Particulate and solid carbon emissions were significantly reduced when the engine was fueled with blends of methyl and isopropyl esters. A 50% blend of the isopropyl ester with low sulfur No. 2 diesel fuel gave the greatest reduction in particulate and solid carbon emissions. However, the soluble organic fraction for the particulates increased with increasing percentage of esters in the fuel blends and this caused increases in the particulate matter at light engine loads. The 70% methyl ester blend with high sulfur No. 2 diesel fuel gave the highest increase in particulate emissions of 53%. The NO_x emissions of all the ester blends were higher than that of No. 2 diesel fuel. The maximum increase was found to be 12% for the 50% isopropyl esters blended with low sulfur No. 2 diesel fuel. The 50 and 70% methyl ester blends showed 3 and 8% increases in NO_x, respectively, compared to No. 2 diesel fuel.

Isigigur et al. [79] performed some tests on a four-cylinder, direct-injection engine using safflower seed oil methyl ester and No. 2 diesel fuel to investigate engine performance and exhaust emissions. In that study, the engine performance of the methyl ester was similar to No. 2 diesel fuel. Lower CO and HC emissions were obtained and a significant decrease was observed in the particulate emissions when the engine was fueled with the methyl ester.

A slight decrease was observed in brake power, brake torque, and brake mean effective pressure values of the engine fueled with methyl ester as compared to No. 2 diesel fuel. They reported that the brake specific fuel consumption and brake thermal efficiency of the engine were slightly higher when the ester was used.

Last et al. [80] measured the emissions from a diesel engine fueled with different blends of soybean oil methyl ester with low sulfur diesel fuel. They noted that at the standard injection timing, emission reductions of HC, CO, and particulate were possible compared to 100% diesel fuel. The NO_x emission increased linearly with the methyl ester fraction. Fuel consumption increased over the full load range, as the fraction of soybean methyl ester became larger. However, depending upon the particular engine calibration and blend ratio, fuel consumption similar to the diesel-fueled engine was possible when measured on a mass basis.

Graboski et al. [81] investigated the effect of blends of soybean oil methyl ester with diesel fuel on engine emissions from a Detroit Diesel Series 60 engine. The fuels were reference diesel fuel, 20, 35, and 65% biodiesel blended with the base diesel fuel and 100% methyl ester. Their results showed that as the percent biodiesel increased, the NO_x emission increased, while HC, CO, and PM decreased. For a 35% biodiesel blend, the NO_x emission increased by only 1% while the particulate emission decreased by 26% relative to the reference diesel fuel. For 100% biodiesel, the NO_x emission increased by 11% while the PM decreased by 66%. The CO and HC emissions were reduced by 47% and 44%, respectively.

Most researchers have observed that vegetable oil esters and their blends with diesel fuel reduce CO, HC, smoke, and particulate emissions. However, they usually cause a slight increase in NO_x emissions relative to No. 2 diesel fuel. The magnitudes of the emission changes appear to be engine dependent. The engine performance of these fuels is also comparable to diesel fuel.

2.8. Diesel Engine Emissions Fueled with Restaurant Waste Oils

This section reviews previous research on using restaurant waste oils as fuels for diesel engines. Engelman et al. [51] investigated using waste soybean oil obtained from Ohio State University cafeteria deep fat fryers directly in a 6-cylinder, turbocharged diesel engine. The authors did not indicate whether the engine had direct fuel injection or not. The waste oil was filtered twice to remove food particles and then heated to about 120°C to 140°C to drive out any water entrained in the oil before use in the diesel engine at 100% waste oil and 10%, 20%, 30%, 40%, and 50% blends with No. 1 diesel and No. 2 diesel. The fuel consumption was lowest with the 20% blend for the higher RPM ranges at full load. At lower RPM, the fuel consumption decreased with increasing waste oil in the blend. Since this result was unexpected, the authors concluded that further investigation was needed. The lowest smoke readings at all speeds were obtained with a 20% waste oil blend. They observed some carbon deposits on the fuel injectors after almost 50 hours of testing but noted that the deposits were not hard deposits. They concluded that waste soybean oil could be used as a diesel fuel extender. The waste soybean oil could be used at different blends with diesel fuel for short periods without engine modifications.

Lague et al. [52] tested 20% and 50% blends of used deep fat frying vegetable oil with diesel fuel and compared its performance with No. 2 diesel fuel after 200 hours of engine operation by using a small indirect-injection (swirl-chamber) diesel engine. Before testing they heated the cloudy blends above 30°C to avoid fuel filter clogging and filtered them to remove any food particles. They found that the thermal efficiencies were not significantly different for any of the fuels tested at the same operating conditions. The average brake specific fuel consumption (BSFC) showed that a 20% blend allowed an 18% savings in diesel fuel and a 50% blend allowed only a 47% diesel fuel savings because the waste vegetable oil heat content (39500 kJ/kg) was lower than for the diesel fuel. In this study, the fuel blends did not cause more deposits than diesel fuel and no piston ring sticking was observed. The deposits were darker as the percentage of waste oil in the blend increased but were not harder to remove. Combustion efficiency did not drop during testing for all the fuels tested. Their results showed that deep frying vegetable oil at 20% and 50% blends gave no fuel-related problems. They concluded that it could be used for long-term use in diesel engines.

Kouremenos et al. [53] studied waste olive oil to determine the effects of waste olive oil/diesel fuel blends on engine performance and emissions. A single cylinder, four stroke, naturally aspirated, indirect-injection (divided chamber) diesel engine was used in that study. They tested 0, 25, 50, and 100% waste olive oil with diesel fuel under varying load conditions. The waste oil's heating value and specific gravity were 37000 kJ/kg and 0.93, respectively. It was observed that the fuel consumption increased when using the blends. The CO and HC emissions increased but a small decrease was observed in NO_x when using the blends.

Karaosmanoglu et al. [54] prepared 10-90% blends (by volume) of filtered, used canola oil and No. 2 diesel fuel to compare engine performance and exhaust emissions with baseline No. 2 diesel fuel. The engine tests were conducted at different speeds at full load and half load conditions by using a Hercules D-2000 NA/DI model, naturally aspirated, direct injection, four cylinder, marine type diesel engine. They reported that, in general, the 20% blend displayed engine performance characteristics that were very similar to diesel fuel and some improvements were observed in exhaust emissions. The blends had no significant effect on carbon deposit formation on the injector nozzles for the short-term engine run.

Cigizoglu et al. [55] used a Daimler Benz OM horizontal, six cylinder, indirect injection (precombustion chamber) diesel engine to investigate the effect of a 20% blend of used sunflower oil with No. 2 diesel fuel on full load engine performance and emissions at several speed levels. At high speeds and full load, the fuel consumption of the blend was found to be close to that of diesel fuel. Significant decreases were observed in smoke levels when using the blend. The power produced at different speed levels did not show a difference for either diesel fuel or the blend at full load.

The research described above has focused on the use of raw waste or used oils as a diesel fuel extender. Most of the engines used in these studies were indirect injection type diesel engines and they are generally more tolerant of changes in fuel viscosity. However, since most modern diesel engines are direct injection type engines, a fuel viscosity closer to diesel fuel is needed. Therefore, most researchers have focused on transesterification of the waste vegetable oils and their use in diesel engines. The following section discusses previous research in this area.

2.9. Diesel Engine Emissions Fueled with Waste Vegetable Oil Esters

Transesterified waste oils are still considered to be biodiesel. There is some experience with these fuels, as will be described below, but generally the feedstocks had fairly low free fatty acid levels. Mittelbach et al. [25] prepared methyl esters from used frying oil and compared their fuel properties to Austrian standards valid for rapeseed oil methyl ester. The amount of free fatty acids in the oils was between 0.26 to 2.12%. After filtration at 40°C to remove solid particles, the oil was transesterified using alkaline catalysis. They noted that all specification values could be met by the used vegetable oil esters except the cold filter plugging point, which in most cases was over –8°C.

Isigigur et al. [66] prepared 0, 10, and 20% blends (by volume) of methyl ester of used frying oil with No. 2 diesel fuel to compare their fuel properties. They found that the heating value and cetane number were a little lower than for No. 2 diesel fuel. The fuel properties of the 10 and 20% blends of the ester with diesel fuel were within the range of those for pure No. 2 diesel fuel.

Mittelbach and Tritthart [67] prepared methyl esters from used frying oil to investigate the effects of the ester on diesel engine exhaust emissions. They measured slightly lower HC, CO, and particulate emissions but increased NO_x values when the ester fuel was used. They found higher fuel consumption for the ester compared with No. 2 diesel fuel due to its lower calorific value.

Nye et al. [43] investigated the esters of used frying oil to determine their effects on engine performance and emissions. The esters of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-ethoxyethanol were prepared using sulfuric acid and potassium hydroxide as acid and base catalysts, respectively. They found that all of the acid-catalyzed fuels had low viscosities, and all of the base-catalyzed fuels had higher viscosities, except for the methanol-based fuel, which was the least viscous of all the fuels. The authors noted that the viscosity measurements of the esters correlated with the percentage of ester yield. In that study, the three fuels with the lowest viscosity, methyl ester prepared with base catalyst, ethyl ester prepared with acid catalyst, and butyl ester prepared with acid catalyst, were tested in half-hour runs in a MWM high-speed diesel engine, and no problems were observed with regard to starting at 25°C, smoothness of running, or smokiness of exhaust. They also tested the methyl and ethyl esters in a Perkins P6 low speed diesel engine and no problems were observed in that engine, either.

Peterson et al. [68] conducted engine testing to compare the engine performance and emissions of ethyl esters produced from waste hydrogenated soybean oil and No. 2 diesel fuel. In this study, two types of engine were used. For the engine performance tests, a direct injected, four cylinder John Deere 4239T-turbocharged diesel engine was used. For the emissions testing, a 1994 Dodge pickup equipped with a direct injected, turbocharged and intercooled, 5.9 L Cummins diesel engine was used. The ester fuel had a higher specific gravity and 1.9 times the viscosity of No. 2 diesel fuel at 40°C. The heat of combustion and sulfur content for biodiesel from waste hydrogenated soybean oil were 12% and 36% lower than for diesel fuel, respectively. The smoke opacity was 71% lower and the engine power was 4.8% lower when the engine was operated with biodiesel compared with diesel fuel. The peak engine torque was reduced by 6% and 3.2% at 1700 and 1300 rpm, respectively. The fuel consumption for the biodiesel fuel was 7% higher than that of No. 2 diesel fuel. There was no significant difference in the thermal efficiencies. Emissions tests showed a 54% decrease in HC, a 46% decrease in CO, a 14.7% decrease in NO_x, a 0.57% increase in CO_2, and a 14% increase in PM when biodiesel was used.

Reed et al. [82] converted waste cooking oils to methyl and ethyl esters for use as an alternative oxygenated diesel fuel substitute. Thirty and 100% blends of ester were tested in a diesel-powered bus on a chassis dynamometer to compare with diesel fuel. No significant difference in power and performance were observed except for the visible reduction of smoke on acceleration with the esters of the used oil. They also tested smoke opacity on diesel fuel, 100% ester, and a 30% blend of ester in diesel fuel, and found that the smoke was reduced to 60% of the diesel value by the 30% blend and to 26% of the diesel value by the pure ester.

In general, almost all of the fuel properties of the biodiesel produced from waste vegetable oil could be brought within the specifications for biodiesel produced from virgin vegetable oil. As with biodiesel from virgin vegetable oils, biodiesel from waste oils causes a significant reduction in CO and PM emissions from diesel engines. With one exception, it also caused the NO_x emissions to increase. The fuel consumption for the esters is higher compared with No. 2 diesel fuel due to its lower calorific value. There is no significant difference in the thermal efficiency and the engine performance compared to No. 2 diesel fuel.

3. EXPERIMENTAL METHODS AND APPARATUS

The main objective of this study was to produce biodiesel from high FFA feedstock and to study the impact of the biodiesel on exhaust emissions and engine performance and to compare to No. 2 diesel fuel and soybean oil methyl ester. In this chapter, the equipment that was used to accomplish the objectives will be discussed. The first section describes the equipment used for the laboratory-scale biodiesel production. The second section describes the engine setup and test schedule. In the last section, the data acquisition system and emission measurement equipment are presented.

3.1. Test System Setup for Small Scale Biodiesel Production

To understand the effects of molar ratio, reaction temperature, reaction time, and catalyst amount on the yield of acid-catalyzed methyl ester, the experimental setup shown in Figure 3.1 was used. The equipment includes a 1000 cc glass container with a hot plate and stirrer, a thermocouple, a thermocouple reader, and a water condenser. The maximum reaction temperature, 60°C, was selected because it is just slightly below the boiling point of methanol so the reaction vessel does not need to be pressurized. During the reaction, any evaporated methanol will be returned to the glass container by the condenser. The mixture was stirred at the same rate for all runs. This system was used for investigating acid-catalyzed pretreatment of high FFA level feedstocks. Then, after the FFA level had been reduced to less than 1%, the same setup was used for alkaline-catalyzed transesterification without heating or condensing.

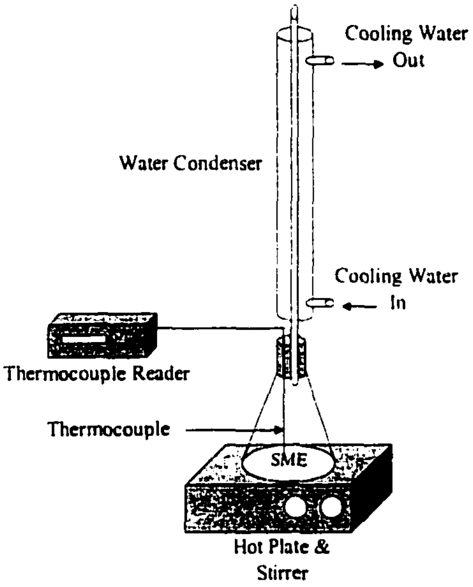


Figure 3.1: Schematic diagram of the small-scale transesterification system setup

3.2. Diesel Engine Setup and Test Schedule

This study included an investigation of the impact of the biodiesel prepared from yellow grease on engine performance and exhaust emissions and comparisons were made to biodiesel from soybean oil and No. 2 diesel fuel. A John Deere 4276T, four-cylinder, four-stroke, turbocharged diesel engine was used for this purpose. The engine was connected to a 150 HP General Electric (Schenectady, NY) model TLC 2544 direct current dynamometer. The combustion system of the diesel engine was a bowl-in-piston, direct-injection, medium-swirl type. The engine was equipped with a distributor type fuel pump. The fuel injectors have four 0.305-mm diameter holes with an opening pressure of 207 bar. The basic specifications of the engine are shown in Table 3.1.

Two different fuel blends (20% and 100%) were prepared with yellow grease methyl ester in No. 2 diesel fuel, and soybean oil methyl ester in No. 2 diesel fuel. The No. 2 diesel fuel was purchased from a commercial supplier. The blends were tested at full load (100%) at 1400-rpm engine speed where the engine torque was 190-ft-lbf. The tests were performed at steady state conditions. The fuels were tested in random order and each test was repeated 3 times. The results were averaged to decrease the uncertainty. The test matrix is shown in Table 3.2.

Table 3.1: Specifications of John Deere 4276T model diesel engine

Bore	106.5 mm
Stroke	127.0 mm
Connecting Rod Length	202.9 mm
Compression Ratio	16.8:1
Maximum Power	57.1 kW @ 2100 rpm
Peak Torque	305.0 Nm @ 1300 rpm

Table 3.2: The engine test conditions and fuel blends

Repetition	*Fuel Type*
First (Full Load at 1400 rpm)	No. 2 Diesel Fuel
	20% Yellow Grease Methyl Ester & 80% No. 2 Diesel Fuel
	Yellow Grease Methyl Ester
	20% Soybean Oil Methyl Ester & 80% No. 2 Diesel Fuel
	Soybean Oil Methyl Ester
Second (Full Load at 1400 rpm)	No. 2 Diesel Fuel
	20% Yellow Grease Methyl Ester & 80% No. 2 Diesel Fuel
	Yellow Grease Methyl Ester
	20% Soybean Oil Methyl Ester & 80% No. 2 Diesel Fuel
	Soybean Oil Methyl Ester
Third (Full Load at 1400 rpm)	No. 2 Diesel Fuel
	20% Yellow Grease Methyl Ester & 80% No. 2 Diesel Fuel
	Yellow Grease Methyl Ester
	20% Soybean Oil Methyl Ester & 80% No. 2 Diesel Fuel
	Soybean Oil Methyl Ester

3.3. Data Acquisition System and Emission Measurement Equipment

In the engine test, two pressure transducers, a Kistler Model 6061B and a Model 6230M1, were installed in the engine cylinder head and the number one cylinder injection line to measure cylinder and injection pressure data, respectively. The specifications of these pressure transducers are shown in Appendix D. Two charge amplifiers, both of which were PCB Piezotronics Model 462A, amplified the pressure signals. High-speed data were acquired using a Labview program and a National Instruments data acquisition system Model AT-M1O-16E-10 board, and the data were stored in a Pentium II computer for analysis. A BEI Electronics, Inc. Model H-25 optical shaft encoder, supplied the engine crank angle signal.

A schematic diagram of the exhaust emission measurement system is shown in Figure 3.2. Calibration of each analyzer was done before each test. The calibration curves are shown in Appendix E. Using the appropriate calibration curve, the measurement error for each analyzer was reduced to less than 2%, as was recommended in the exhaust analyzer bench manual. In the measurements of the engine exhaust emissions, the following instruments were used:

- Rosemount Analytical, Inc., model 755R non-dispersive infrared O_2 monitor,
- Rosemount Analytical, Inc., model 880A non-dispersive infrared CO analyzer,
- Rosemount Analytical, Inc., model 880A non-dispersive infrared CO_2 analyzer,
- J.U.M. Engineering, model VE7, flame ionization detector (FID), HC analyzer,
- Beckman Industrial Corp., model 955 chemiluminescent NO/NO_x analyzer, and
- Robert Bosch GMBH, model ETD02050 smoke meter.

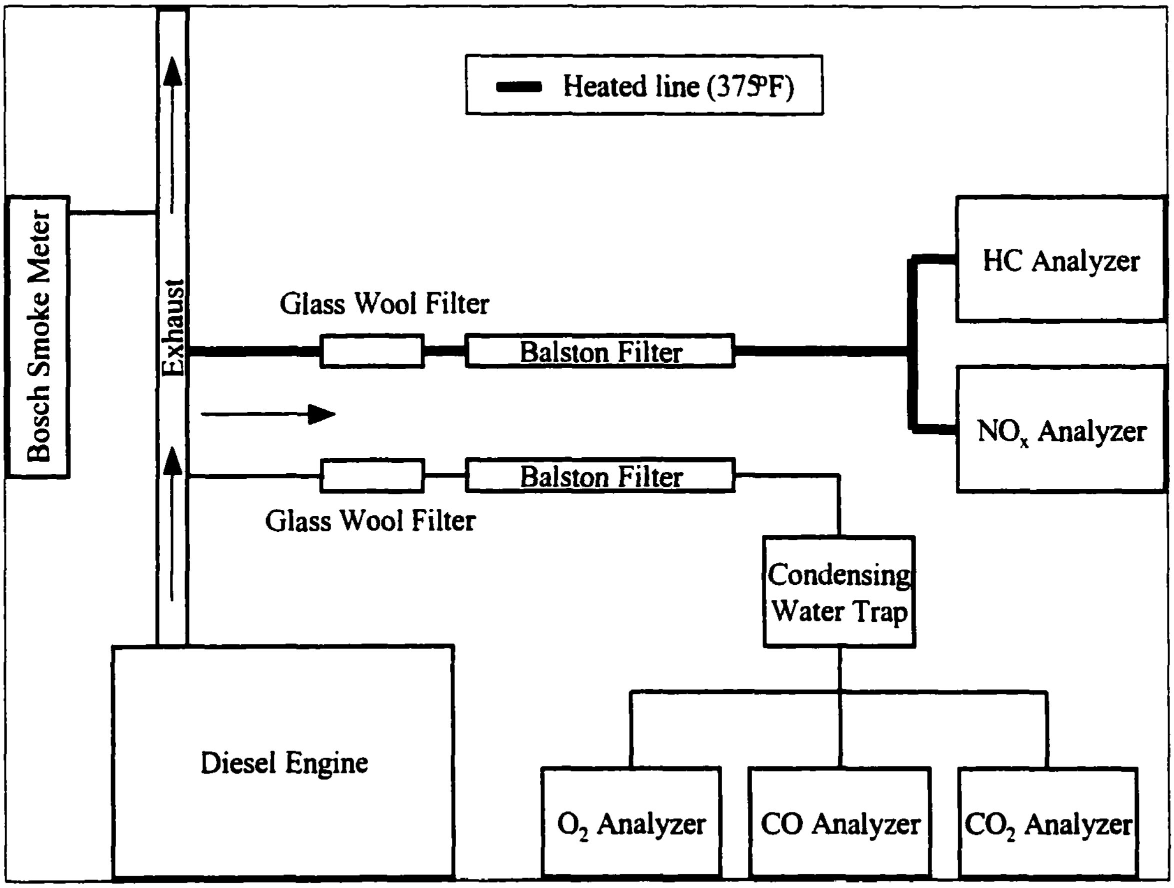


Figure 3.2: Schematic diagram of exhaust emission measurement system

4. DATA ANALYSIS AND CALCULATION

One of the main tasks of this study was to compare the engine performance and emission levels among the fuels used in the diesel engine. In this chapter, the engine data calculations and statistical analysis will be discussed. The first section discusses the data analysis of the exhaust emissions and the humidity correction factor for NO_x. The second section describes the cylinder and injection pressure analysis. The third section presents the heat release analysis that was used to determine the start of combustion. In the last section, the statistical analysis methods performed on the data for engine performance and emissions are presented.

4.1. Data Analysis

To compare the engine performance and emission results for biodiesel from a high FFA feedstock (yellow grease) with biodiesel from soybean oil and with No. 2 diesel fuel, the data were converted to the units of g/kW-hr, known as a "brake specific" basis. This is the most common way to present emissions data since it is easy to compare brake specific values between engines of different size. To do this conversion, it is necessary to develop a balanced chemical equation of the combustion reaction. The first section describes this exhaust emission calculation process. Then, the second section discusses the humidity correction factor for NO_x.

4.1.1. Exhaust Emissions

The chemical combustion equation for diesel fuel is required to convert the measured exhaust emissions to brake specific emissions. A general chemical equation is shown below for the complete combustion of an oxygenated hydrocarbon fuel.

$$C_xH_yO_z + A\,(0.21\,O_2 + 0.79\,N_2) \rightarrow B\,(y_{CO2,\,dry}\,CO_2 + y_{O2,\,dry}\,O_2 + y_{N2,\,dry}\,N_2) + D\,(H_2O) \qquad (4\text{-}1)$$

where x = number of carbon atoms in the fuel molecule

y = number of hydrogen atoms in the fuel molecule

z = number of oxygen atoms in the fuel molecule

$y_{i,\,dry}$ = mole fraction of a chemical species on the dry basis

A = air-fuel ratio (molar)

B = number of moles of dry products per mole of fuel

D = number of moles of water per mole of fuel

In this equation, B and D can be calculated by atomic balance. Therefore

$$B = A + (z/2) - (y/4) \qquad (4\text{-}2)$$

$$D = y/2 \qquad (4\text{-}3)$$

Now B and D can be used to find the brake specific (BS) emissions. The brake specific equations for each gaseous species are as follows.

$$\begin{aligned} BS_{CO} &= [\text{kmol CO / kmol dpg}] * [\text{kmol dpg / kmol fuel}] * [\text{kmol fuel / kg fuel}] \\ &\quad * [\text{kg fuel / hr}] * [\text{kg CO / kmol CO}] * [1 / P_b] \qquad (4\text{-}4) \\ &= [y_{co,\,dry}] * [B] * [1 / MW_{fuel}] * [m_{fuel}] * [MW_{co}] * [1 / P_b] \\ &= \text{kg CO/ kW-hr} \end{aligned}$$

$$\begin{aligned} BS_{CO2} &= [\text{kmol CO}_2\text{ / kmol dpg}] * [\text{kmol dpg / kmol fuel}] * [\text{kmol fuel / kg fuel}] \\ &\quad * [\text{kg fuel / hr}] * [\text{kg CO}_2\text{ / kmol CO}_2] * [1 / P_b] \qquad (4\text{-}5) \end{aligned}$$

$$BS_{NO} = [\text{kmol NO / kmol wpg}] * [\text{kmol wpg / kmol fuel}] * [\text{kmol fuel / kg fuel}]$$
$$* [\text{kg fuel / hr}] * [\text{kg NO / kmol NO}] * [1 / P_b] \qquad (4\text{-}6)$$

$$BS_{NOx} = [\text{kmol NO}_x\text{ / kmol wpg}] * [\text{kmol wpg / kmol fuel}] * [\text{kmol fuel / kg fuel}]$$
$$* [\text{kg fuel / hr}] * [\text{kg NO}_x\text{ / kmol NO}_x] * [1 / P_b] \qquad (4\text{-}7)$$

$$BS_{HC} = [\text{kmol HC / kmol wpg}] * [\text{kmol wpg / kmol fuel}] * [\text{kmol fuel / kg fuel}]$$
$$* [\text{kg fuel / hr}] * [\text{kg HC / kmol HC}] * [1 / P_b] \qquad (4\text{-}8)$$

where dpg = dry product gas

wpg = wet product gas

MW = molecular weight

m_{fuel} = fuel flow rate (kg/hr)

P_b = brake power (kW)

kmol = kilo mole

The molecular weights of the blends of ester and diesel fuel can be calculated as follows:

$$MW_{blend} = y_d * MW_{diesel} + y_e * MW_{ester} \qquad (4\text{-}9)$$

where MW_{blend} = molecular weight of the fuel blend

MW_{diesel} = molecular weight of the diesel fuel

MW_{ester} = molecular weight of the ester

y_d = mole fraction of the diesel in the fuel blend

y_e = mole fraction of the ester in the fuel blend

And x, y, and z for carbon, hydrogen, and oxygen atom number for the fuel blends, respectively, can be obtained in the following way;

$$\begin{aligned} x &= y_d * N_{Cdiesel} + y_e * N_{Cester} \\ y &= y_d * N_{Hdiesel} + y_e * N_{Hester} \\ z &= y_d * N_{Odiesel} + y_e * N_{Oester} \end{aligned} \tag{4-10}$$

where $N_{Cdiesel}$ = carbon atom number in the diesel fuel

N_{Cester} = carbon atom number in the ester

$N_{Hdiesel}$ = hydrogen atom number in the diesel fuel

N_{Hester} = hydrogen atom number in the ester

$N_{Odiesel}$ = oxygen atom number in the diesel fuel

N_{Oester} = oxygen atom number in the ester

4.1.2. Humidity Correction Factor for NO_x

The Society of Automotive Engineers [83] recommends that a NO_x humidity correction factor be used since the engine intake air contains some humidity. The specific humidity of the air, h, is computed from following equation.

$$h = \frac{621.10 * P_v}{P_b - P_v} \tag{4-11}$$

where h = specific humidity (g H_2O / kg dry air)

P_b = observed barometric pressure (kPa)

P_v = partial pressure of water vapor (kPa)

The partial pressure of water vapor, P_v, can be calculated from Ferrel's equation [84].

$$P_v = P_w - 1.80\,A * P_b\,(T_d - T_w) \tag{4-12}$$

where P_w = saturation pressure of water vapor at the wet bulb temperature (kPa)

T_d = dry bulb temperature (°C)

T_w = wet bulb temperature (°C)

A = an experimentally derived constant, = $3.67 * 10^{-4}\,(1 + 0.001152 * T_w)$

The saturation pressure of water vapor at the wet bulb temperature can be obtained from a least square fit to Keenan and Keye's steam table [85].

$$P_w = 0.6048346 + 4.59058 * 10^{-2}\,T_w + 1.2444 * 10^{-3}\,T_w^{\,2} + 3.52248 * 10^{-5}\,T_w^{\,3} + 9.32206 * 10^{-8}\,T_w^{\,4} + 4.18128 * 10^{-9}\,T_w^{\,5} \tag{4-13}$$

Now, the corrected NO_x concentration can be calculated as [80]:

$$[NO]_{corr} = [NO]_{wet} * \frac{1}{k} \tag{4-14}$$

where $[NO]_{corr}$ = corrected NO concentration (ppm)

$[NO]_{wet}$ = measured NO concentration on a wet basis (ppm)

$k = 1 + 7\,A\,(h\text{-}10.714) + 1.8\,B\,(T\text{-}29.444)$

A = 0.044 (F/A) – 0.0038

B = -0.116 (F/A) + 0.0053

T = intake air temperature (°C)

F/A = fuel air ratio (dry basis)

4.2. Analysis of Injection Pressure Cylinder Pressure and Ignition Delay

Measurements of the engine cylinder pressure and fuel injection pressure were taken using the same procedure. Two sets of data were taken at each run for injection and cylinder pressure. To eliminate the random noise, a large number of cycles were collected. Both data sets consisted of fifty cycles of averaged data taken every ¼ of a degree. The data acquisition system provided the voltage levels corresponding to the pressure values. Then, these voltage levels were converted to pressure units. The injection pressure data were used to estimate the fuel injection timing and the cylinder pressure data were used to calculate heat release rates and the start of combustion.

A sample of the fuel injection pressure profiles is shown in Figure 4.1. These measured pressures may not be exactly the same as the actual pressure at the nozzle tip since the pressure is measured in the line, several inches away from the nozzle tip. The profiles show the pressure waves which move back and forth in the injection line [86].

A sample of the cylinder pressure profiles is shown in Figure 4.2. Since, the piezoelectric transducers do not hold an absolute pressure, it was necessary to establish an absolute reference pressure. The pressure at the bottom dead center before compression was assumed to be equal to the intake manifold pressure, following the techniques of Lancaster et al. [87].

The definition of the ignition delay in a diesel engine is the time between the start of fuel injection and the start of combustion. The start of injection is usually taken as the time when the injector needle lifts off its seat. Instrumentation to directly measure the timing of this event was not available so an alternative method to determine the start of injection was needed. Measurement of the injector needle opening pressure had shown that fuel would be

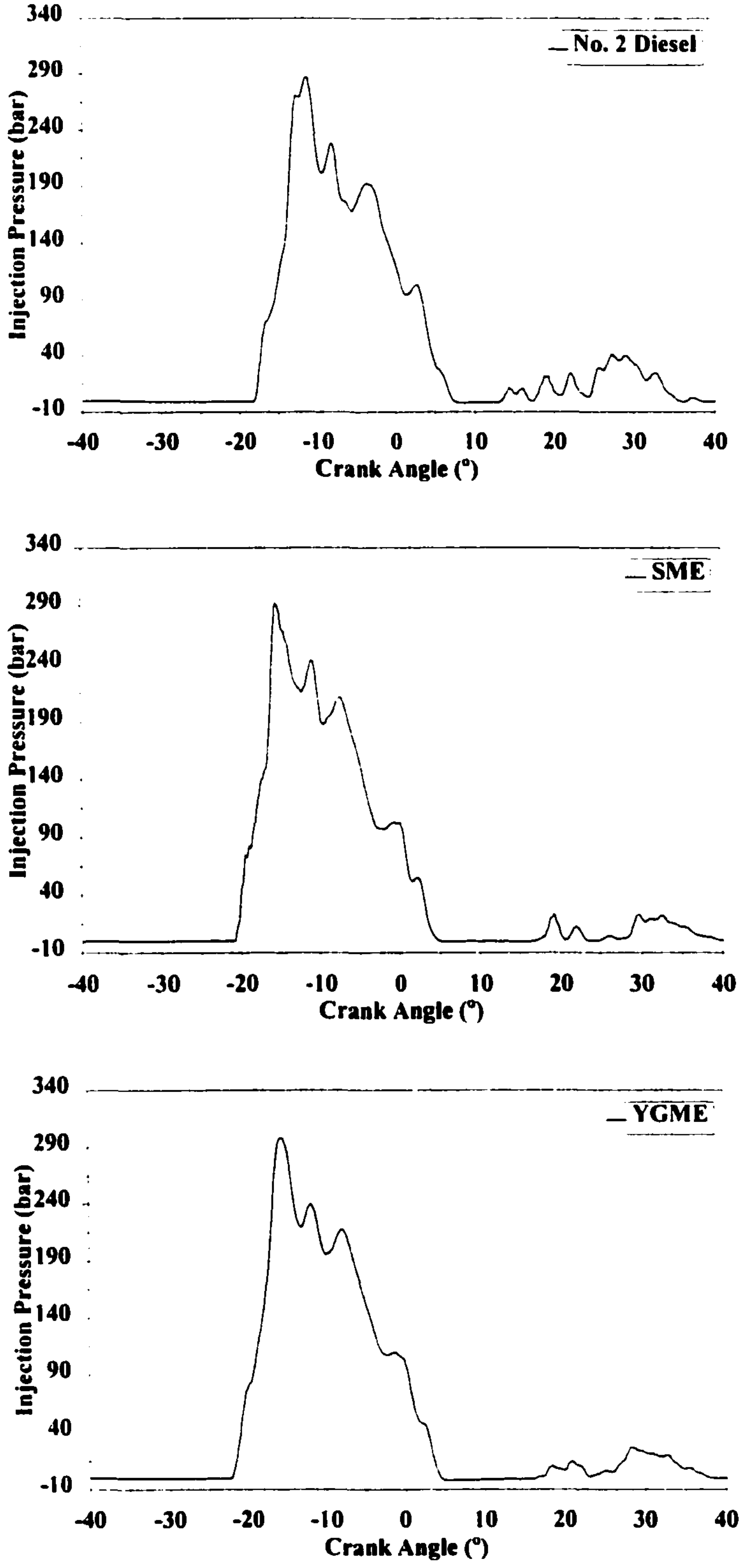


Figure 4.1: Sample of injection pressure profiles

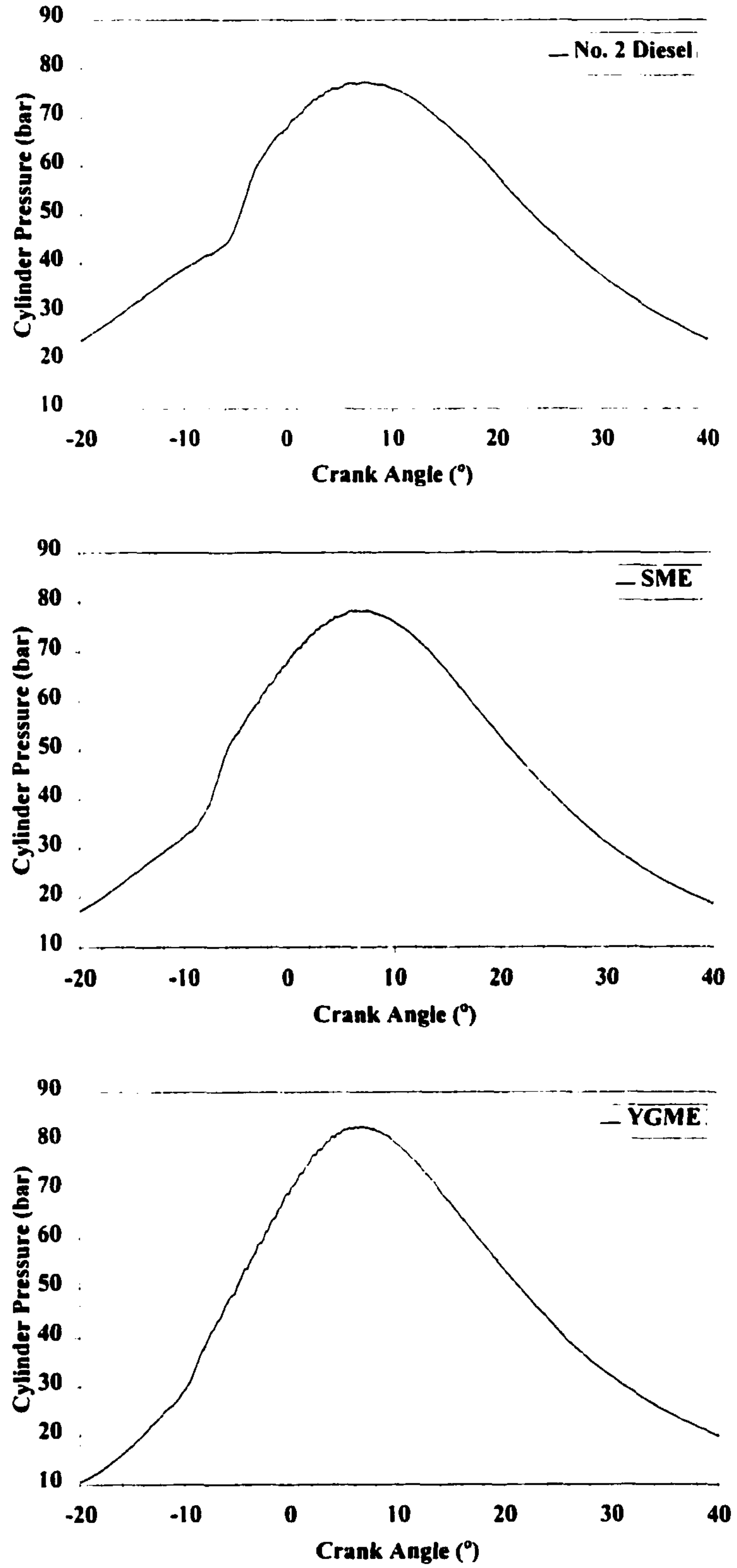


Figure 4.2: Sample of cylinder pressure profiles

injected into the cylinder at an injection line pressure of 207 bar [78]. The time when the measured injection line pressure reached this pressure was taken to be the start of fuel injection. The start of combustion is more difficult to determine precisely, since three possible definitions of ignition delay have been defined by Henein and Bolt [88]. The first is the illumination delay, which is the time between the start of injection and the start of the luminous flame in the engine. The second is the temperature rise delay, which is the time from the start of injection to a specified cylinder-average temperature rise due to combustion. The third is the pressure rise delay, which is the time between the start of injection and a specified pressure rise due to combustion. However, Van Gerpen [89] suggested an alternative way to determine ignition delay. He proposed that the rate of heat release be used as the basis for the start of combustion. For this method, the start of combustion was defined in terms of the change in the slope of the heat release rate that occurs at the time of ignition.

For the current study, the ignition delay was calculated as the time between when the injection pressure line reached 207 bar and when the change occurred in the slope of the heat release rate at the point of ignition.

4.3. Heat Release Analysis and Cylinder Pressure Smoothing Technique

Engine cylinder pressure data were used to evaluate the rate of heat release. In this study, a simplified version of the heat release combustion model of Krieger and Borman [90] was used. In this model, the experimental cylinder pressure data are used to compute an apparent fuel-burning rate. The model assumes thermodynamic equilibrium during combustion in the cylinder, but ignores temperature gradients, pressure waves, nonequilibrium conditions, fuel vaporization, mixing, and so on.

From the first law of thermodynamics

$$\frac{dU}{dt} = \dot{Q} - \dot{W} \tag{4-15}$$

$$mC_v \frac{dT}{dt} = \dot{Q} - P\frac{dv}{dt} \tag{4-16}$$

where $\dot{Q}$ = the combination of the heat release rate and the heat transfer rate across the cylinder wall

$\dot{W}$ = the rate of work done by the system due to system boundary displacement

To simplify equation (4-16) the ideal gas assumption can be used.

$$PV = mRT \tag{4-17}$$

Equation (4-17) can be differentiated (assuming constant mass):

$$\frac{dT}{dt} = \frac{1}{mR}\left[P\frac{dV}{dt} + V\frac{dP}{dt}\right] \tag{4-18}$$

After combining these two equations, the heat release equation becomes:

$$\dot{Q} = \left[\frac{C_v}{R} + 1\right]P\frac{dV}{dt} + \frac{C_v}{R}V\frac{dP}{dt} \tag{4-19}$$

After replacing time (t) with the crank angle (θ), the equation becomes

$$\dot{Q} = \frac{\lambda}{\lambda - 1}P\frac{dV}{d\theta} + \frac{1}{\lambda - 1}V\frac{dP}{d\theta} \tag{4-20}$$

where λ = the ratio of specific heats, C_p/C_v. For diesel heat release analysis, λ is 1.3 to 1.35 [91].

A sample heat release rate profile calculated using the above procedure is shown in Figure 4.3. Due to heat loss from the cylinder and the cooling effect of the fuel vaporizing as it is injected into the cylinder, the heat release rate is slightly negative during the ignition delay period. The initial phase of combustion, called the premixed combustion, is very rapid because of the combustion of the fuel that has mixed with air during the ignition delay. After this phase, the combustion continues slowly until most of fuel is burned. This phase of combustion is called mixing-controlled combustion. The final combustion phase is the late combustion which continues until the end of the expansion stroke.

The heat release rate equation (4-20) contains two derivative terms; the time derivative of the volume and the time derivative of the pressure. The time derivative of volume is an easily calculated quantity. However, calculating the time derivative of pressure is more difficult. Errors in the pressure data or in the differentiation process will significantly affect the heat release rate. Austen and Lyn [92] showed that a 1-degree error in the pressure measurement can cause a 50% error in the heat release rate. Van Gerpen [89] also showed that small oscillations in the pressure data caused errors in the heat release rate curve.

Monyem [78] tested the use of two or three grid points for first-derivative approximations as forward, backward, and central difference representations, but they failed to provide good results. All provided very noisy pressure derivatives. Then Monyem used a four-point difference approximation to differentiate the pressure data and this technique provided a better result. This same method was used in this study to calculate the rate of heat release. The first-derivative approximation using four points was:

$$(du/dx)_i = (-u_{i+2} + 8\,u_{i+1} - 8\,u_{i-1} + u_{i-2}) / (12 * \Delta\theta) \qquad (4\text{-}21)$$

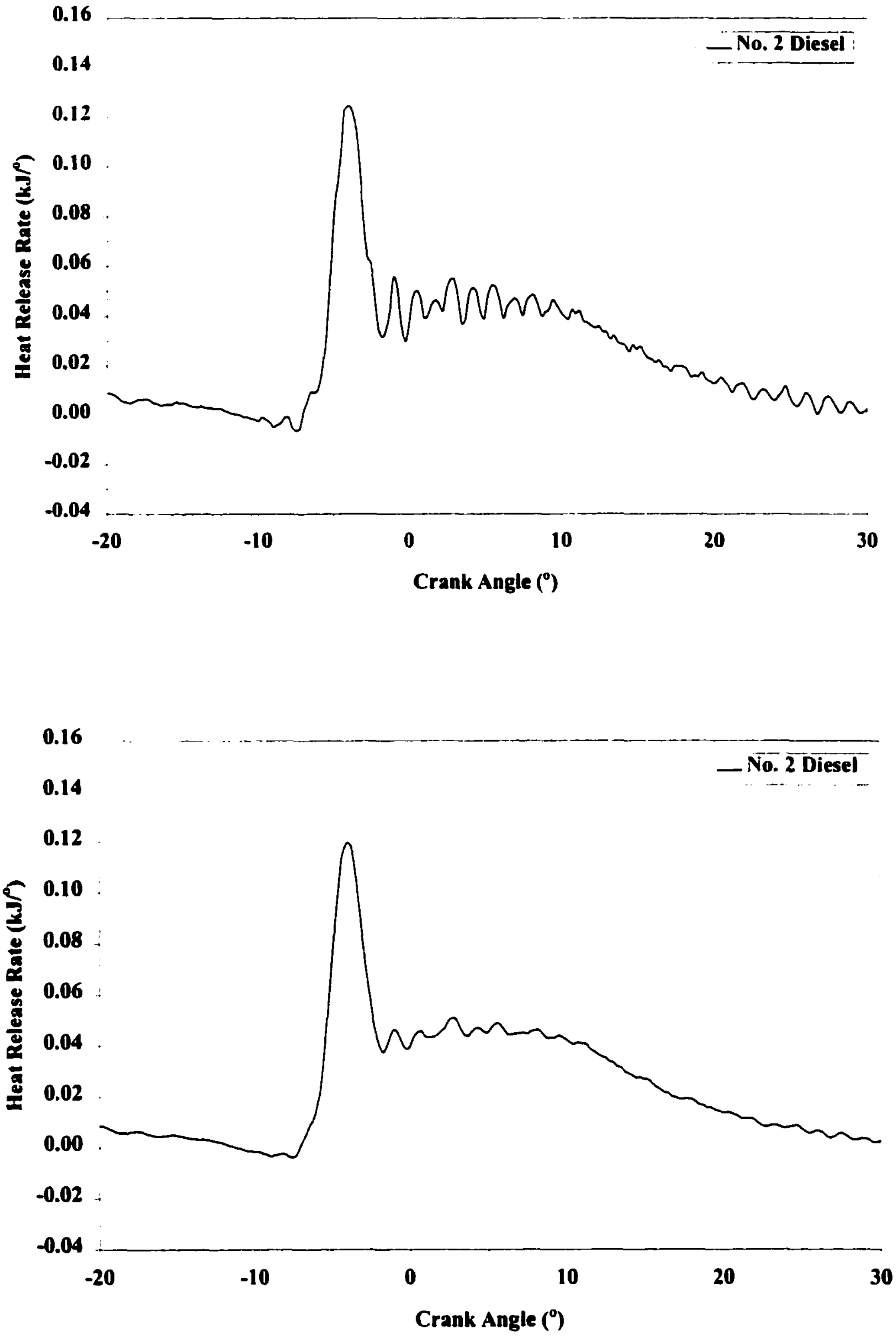


Figure 4.3: Heat release profile before and after filtering

where i = a specific time or crank angle

u_i = pressure at crank angle i

$\Delta\theta$ = crank angle interval between i and i+1

It is also necessary to provide some smoothing of the pressure data to reduce the unwanted noise. A smoothing technique called 'digital filtering' can reduce noise dramatically [89]. Digital filtering is a numerical process where a new set of data is produced which has different frequency characteristics. The digital filtering technique used for this study was as follows.

$$g_i = (f_{i-1} + f_{i+1}) / 2 \qquad (4\text{-}22)$$

$$h_i = (g_{i-1} + g_i + g_{i+1}) / 3 \qquad (4\text{-}23)$$

where f_i = the original data

g_i = intermediate value

h_i = the filtered data

As samples of the smoothing technique used in this study, Figures 4.3, 4.4, and 4.5 show the unsmoothed and smoothed data vs. crank angle for heat release rate, cylinder pressure, and first derivative of cylinder pressure, respectively. The large amplitude oscillations in the cylinder pressure and in the first derivative of the cylinder pressure curves were mostly gone after filtering while the large peak due to the rapid combustion was reduced somewhat but still prominent.

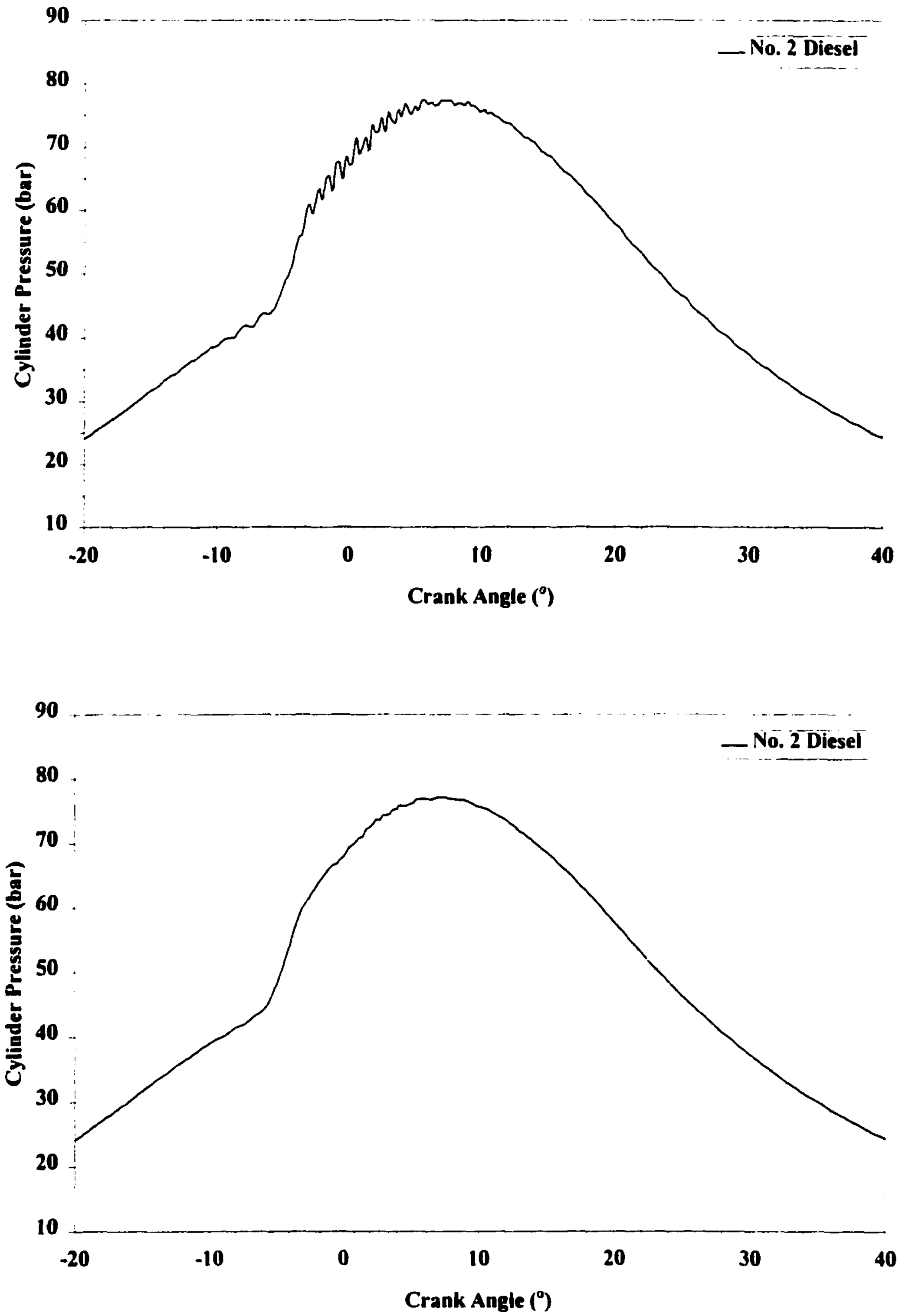
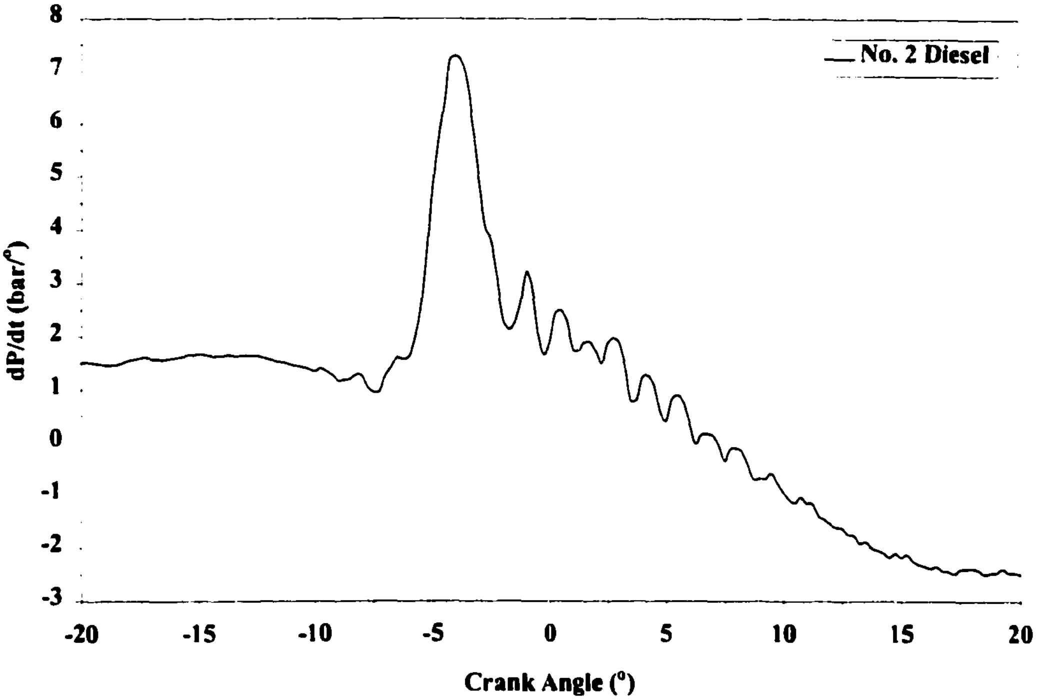


Figure 4.4: Cylinder pressure profile before and after filtering



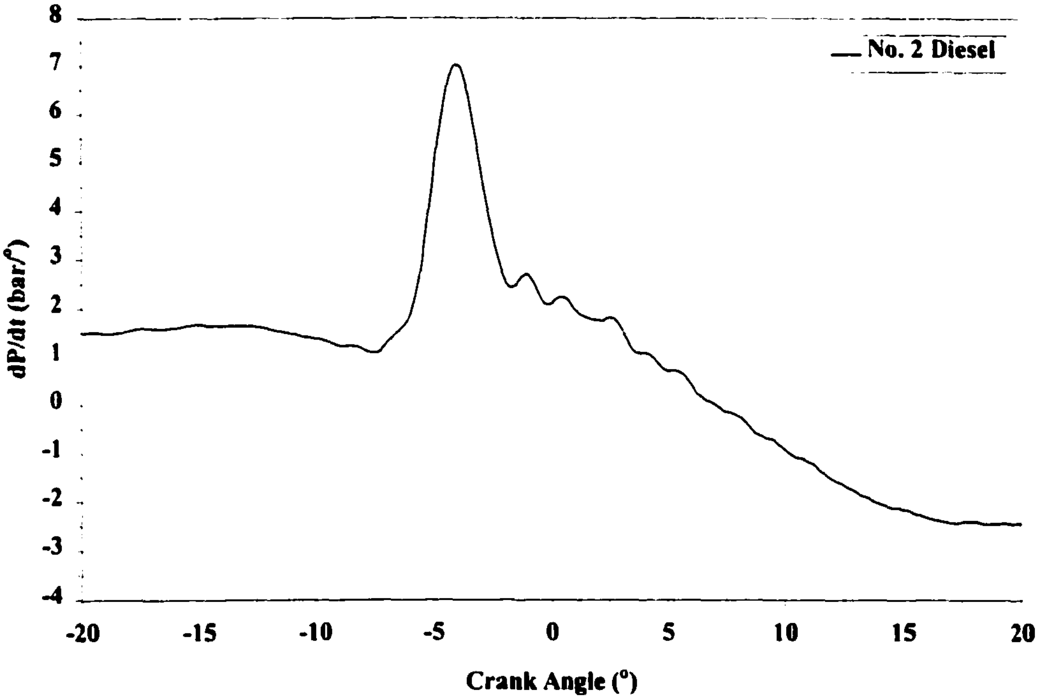


Figure 4.5: Cylinder pressure derivative before and after filtering

4.4. Statistical Analysis

Statistical analyses were performed on the data collected in the engine testing of different fuels. Using analysis of variance (ANOVA) and Tukey's grouping methods, the engine performance and emissions of each fuel were compared to each other to determine whether or not there was a significant difference between the fuels. More extensive explanation of these methods is provided in Ott [93] and Barnes [94]. A significance level of 0.05 (95% confidence interval) was used for the analyses. The Tukey's grouping tables are presented in the Engine Test Results and Discussion chapter. A sample SAS program, written to analyze the collected data, and another form of the statistical analysis data, the ANOVA tables, is also shown in Appendix F for each variable.

5. BIODIESEL PRODUCTION FROM HIGH FFA FEEDSTOCKS

In this chapter, the process development for biodiesel production from high free fatty acid feedstocks will be described. This will be followed by a chapter that discusses the effect of the biodiesel produced from these feedstocks on diesel engine emissions and performance.

Experiments conducted very early in this project showed that feedstocks with high free fatty acid levels could not be transesterified with the alkaline catalysts which have been used with good success for vegetable oils. The alkaline catalyst reacts with the FFAs to form soaps which remove the catalyst from the reaction and prevent the separation of the glycerin and the ester. It was known from the literature that acid catalysts could be used for transesterification and did not have these disadvantages.

While there have been many studies into the use of acid catalysts, and several of those studies were described in the literature review, there have not been any detailed studies of the effects of the various process parameters on the acid catalyzed transesterification reaction. It was determined that conducting such a study was an important first step in developing a process for high FFA feedstocks. In the first part of this chapter, the results of this study into the preparation of methyl esters with sulfuric acid catalyst is presented. The effect of the molar ratio of alcohol, reaction temperature, catalyst amount, reaction time, water, and FFA level on the completion of the acid-catalyzed reaction will be presented.

When the acid catalyzed reaction with vegetable oil feedstocks was understood, the study was extended to feedstocks with elevated levels of FFAs. Since it was difficult to obtain high FFA feedstocks with stable properties and consistent purity, a synthetic high FFA feedstock was studied. This feedstock was prepared by adding a pure FFA to soybean oil.

The results of the tests conducted to investigate the preparation of methyl ester from the material with high FFA using a synthetic mixture are presented here. In that section, the effect of variables such as methanol molar ratio, acid catalyst amount, and reaction time on the reduction of FFA level will be presented. One of the conclusions that will be drawn is that the high FFA feedstocks are most efficiently transesterified by a combination of acid-catalyzed pretreatment followed by an alkaline-catalyzed main reaction.

The final step in the process development was to test the process with actual samples of high FFA feedstocks such as yellow and brown grease. This section also includes the effect of the acid value on the alkaline-catalyzed transesterification reaction. The next two sections discuss preparation of methyl esters from yellow grease and brown grease and compare the simulated high FFA feedstock study and the actual animal fat study and the differences which affect the reactions are discussed. These sections also include the effect of different alkaline catalysts and their amounts on the main transesterification reaction, and on the residual soap and catalyst analysis. The effect of the solubility of the alcohols, the number of steps in the acid-catalyzed pretreatment reaction, and alkaline catalyst type and amounts on the yield will also be discussed. Then, the final sections will describe the implementation of the process into a 50-gallon per day pilot plant. Actual experience with large-scale biodiesel production from soybean oil, yellow grease, and brown grease will be described.

5.1. Preparation of Methyl Ester with Sulfuric Acid Catalyst

One of the tasks of this study was to investigate the effect of process variables on acid-catalyzed transesterification since acid catalysts can be used to esterify material with high FFAs. The variables that affect acid-catalyzed biodiesel were investigated using the small-scale transesterification system described earlier. The molar ratio of alcohol, reaction temperature, catalyst amount, reaction time, and the inhibiting effect of water were investigated to determine the best strategy for producing biodiesel. The soybean oil was purchased from a local food store. The alcohol used was methanol and sulfuric acid was the catalyst. To compare the effect of different alcohol types on ester formation, methanol, ethanol, 2-propanol, and n-butanol were compared. The experimental conditions are given in Table 5.1.

The following procedure was used to prepare acid-catalyzed biodiesel. Solutions of sulfuric acid in methanol were prepared at room temperature. The sulfuric acid percentage was based on the weight of vegetable oil (1%, 3%, and 5%). Then, the solution was added to the vegetable oil at the required temperature (60°C, 45°C, and 25°C) while stirring. The mixture was gently stirred for 48 (or 96) hours at atmospheric pressure and the required

Table 5.1: Reaction conditions for methyl ester preparation

Run No.	*Reaction Temperature (°C)*	*% Catalyst**	*Molar Ratio***	*Reaction Time (hours)*
1	60	3	3.3:1	48
2	60	3	3.9:1	48
3	60	3	6:1	48
4	60	3	20:1	48
5	60	3	30:1	48
6	60	3	6:1	96
7	25	3	6:1	48
8	45	3	6:1	48
9	60	1	6:1	48
10	60	5	6:1	48

* Sulfuric acid.

** Methanol to soybean oil.

temperature. After the reaction period was complete, the ester and glycerin layers were allowed to separate in a separatory funnel. Then, the methyl esters were washed four times with distilled water to remove the excess alcohol and catalyst. Previous studies [14] had shown that four washing cycles is sufficient. Finally, the ester was stirred with around 100 cc of pure glycerin for 15 minutes to extract the residual water in the ester, and then separated again. This glycerin was also to remove some of the polar contaminants such as monoglycerides.

The completeness of the reaction was measured using the American Oil Chemists' Society (A.O.C.S.) Official Method Ca 14-56 known as the Total, Free and Combined Glycerin (Iodometric-Periodic Acid) Method [95]. This method determines the total, free, and combined glycerin in fats and oils. The test procedure is given in Appendix A. The fraction of the original glycerin from the oil that is present in the ester was subtracted from 100% and this quantity was defined to be the *completeness of the reaction.* The specific gravity of the ester at 15.5°C was also measured and recorded after each test as a second indicator of the reaction completeness.

5.1.1. Effect of Molar Ratio

The molar ratio of alcohol to vegetable oil is one of the most important factors that influence the conversion of vegetable oil to its ester. For the stoichiometric reaction, 3 moles of alcohol are required per mole of vegetable oil. In reality, the molar ratio should be higher than the theoretical ratio to drive the reaction to completion. To investigate the effect of molar ratio, five different molar ratios, 3.3:1, 3.9:1, 6:1, 20:1, and 30:1, were selected. Each reaction was run for 48 hours with 3% acid catalyst at 60°C. The changes in conversion and the specific gravity of the methyl esters are shown in Table 5.2 and Figure 5.1. Ester conversions reached a maximum of 98.4% at the 30:1 molar ratio. The specific gravity of the ester decreased somewhat with increasing molar ratio which is probably due to a decrease in residual triglycerides. The maximum and minimum specific gravities were measured at 3.3:1 and 30:1 molar ratios, and were 0.8916 and 0.8840, respectively.

Table 5.2: Effect of molar ratio on ester conversion and specific gravity of ester

Molar Ratio	*Ester Conversion (%)*	*Spe. Gravity of the Ester*
3.3:1	77.2	0.8916
3.9:1	80.6	0.8914
6:1	87.8	0.8876
20:1	96.4	0.8840
30:1	98.4	0.8836

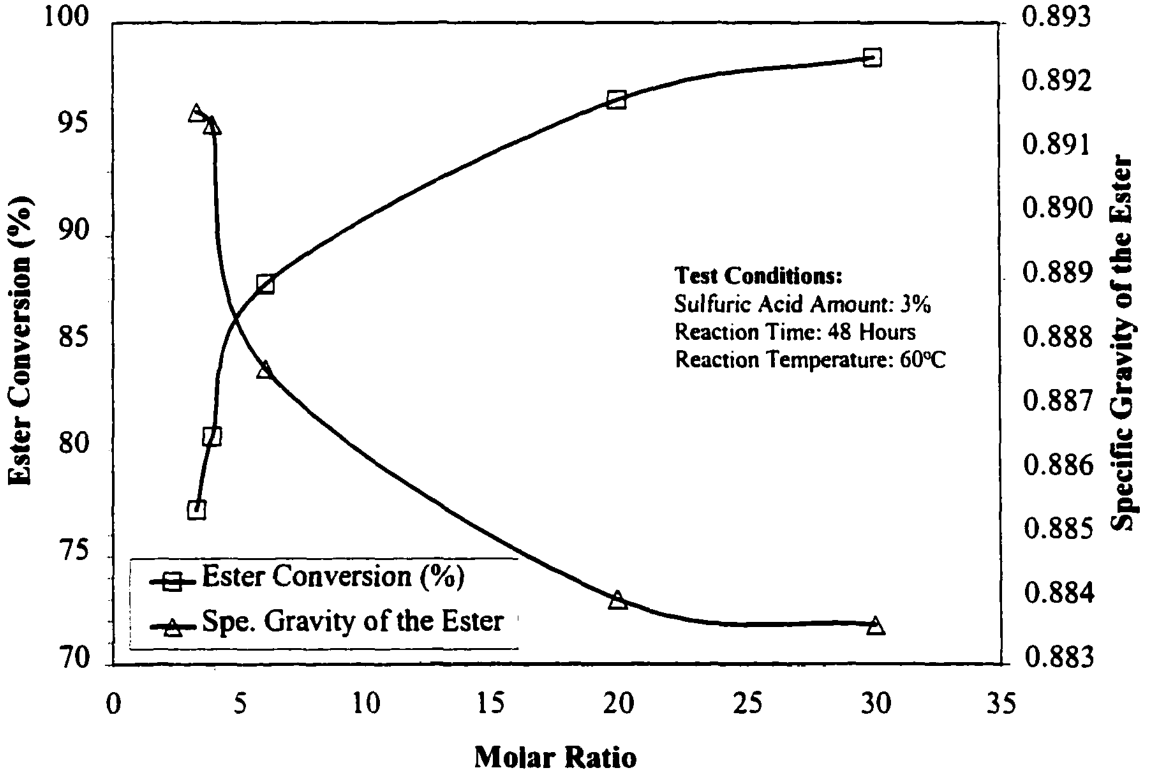


Figure 5.1: Effect of molar ratio on ester conversion

5.1.2. Effect of Reaction Temperature

Another important factor that affects the conversion of vegetable oil to its ester is the reaction temperature. Three different reaction temperatures, 25°C, 45°C, and 60°C, were selected to determine the effect of temperature on ester formation. The highest reaction temperature, 60°C, was selected because it is near the boiling point of methanol. Each reaction was run for 48 hours with 3% acid catalyst and a 6:1 molar ratio test condition. The changes in the ester formation and specific gravity of the methyl ester are shown in Table 5.3 and Figure 5.2. As can be seen, the ester conversion increased with increasing reaction temperature. Ester conversions were 8.3%, 57.2% and 87.8% at 25°C, 45°C, and 60°C, respectively. The specific gravity of the ester decreased with increasing reaction temperature. At 25°C the maximum specific gravity of the methyl ester was 0.9171 which is close to the original specific gravity of the soybean oil. Acid-catalyzed transesterification appears to require temperatures of at least 60°C.

Table 5.3: Effect of reaction temperature on the conversion and specific gravity of ester

Temperature (°C)	*Ester Conversion (%)*	*Spe. Gravity of the Ester*
25	8.3	0.9171
45	57.2	0.8978
60	87.8	0.8876

5.1.3. Effect of Catalyst Amount

The catalyst amount is another important factor that affects the conversion of vegetable oil to its ester. Three different catalyst amounts, 1%, 3%, and 5% sulfuric acid, were selected. These percentages were weight fractions of the oil supplied for the reaction.

For each case, the reaction continued for 48 hours at 60°C with a 6:1 molar ratio of methanol to oil. The relationships between the catalyst amount, the ester formation and specific gravity of the methyl ester are shown in Table 5.4 and Figure 5.3. Ester formation increased with increasing catalyst amount. The ester conversions were 72.7%, 87.8% and 95.0% at 1%, 3%, and 5% sulfuric acid, respectively. The specific gravity of the ester decreased with increasing catalyst amount.

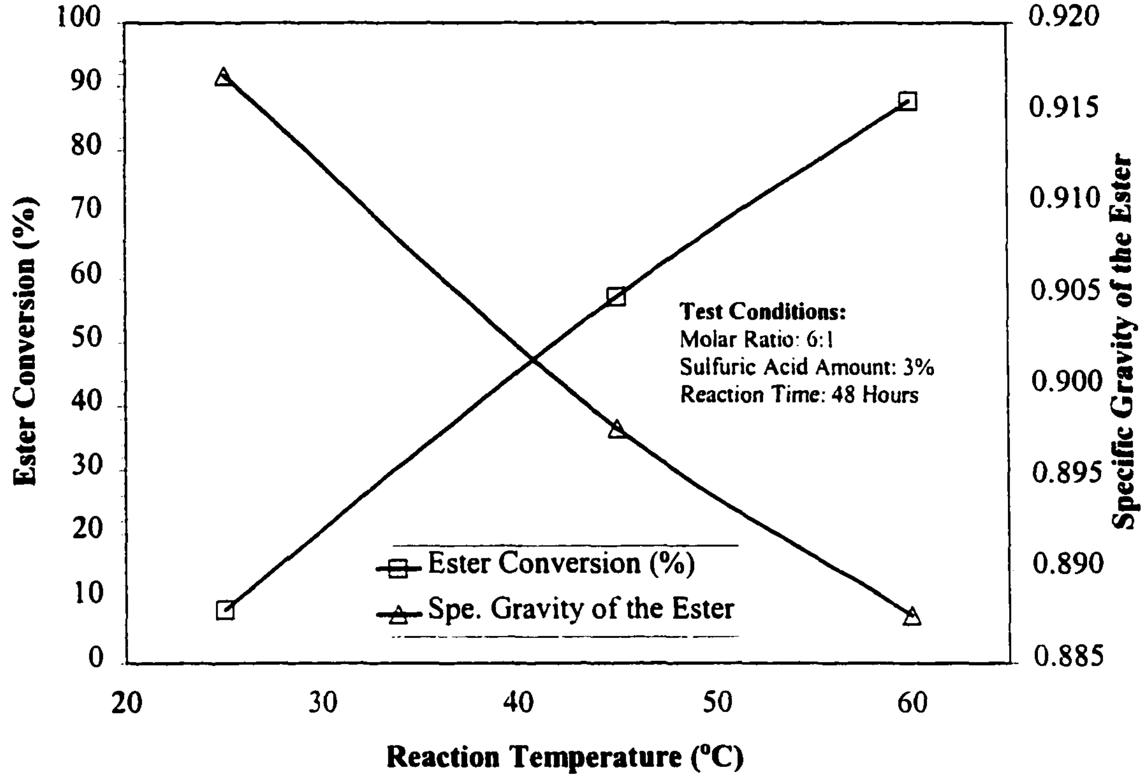


Figure 5.2: Effect of reaction temperature on ester conversion

Table 5.4: Effect of catalyst amount on ester conversion and specific gravity of ester

% Sulfuric Acid	*Ester Conversion (%)*	*Spe. Gravity of the Ester*
1	72.7	0.8933
3	87.8	0.8876
5	95.0	0.8858

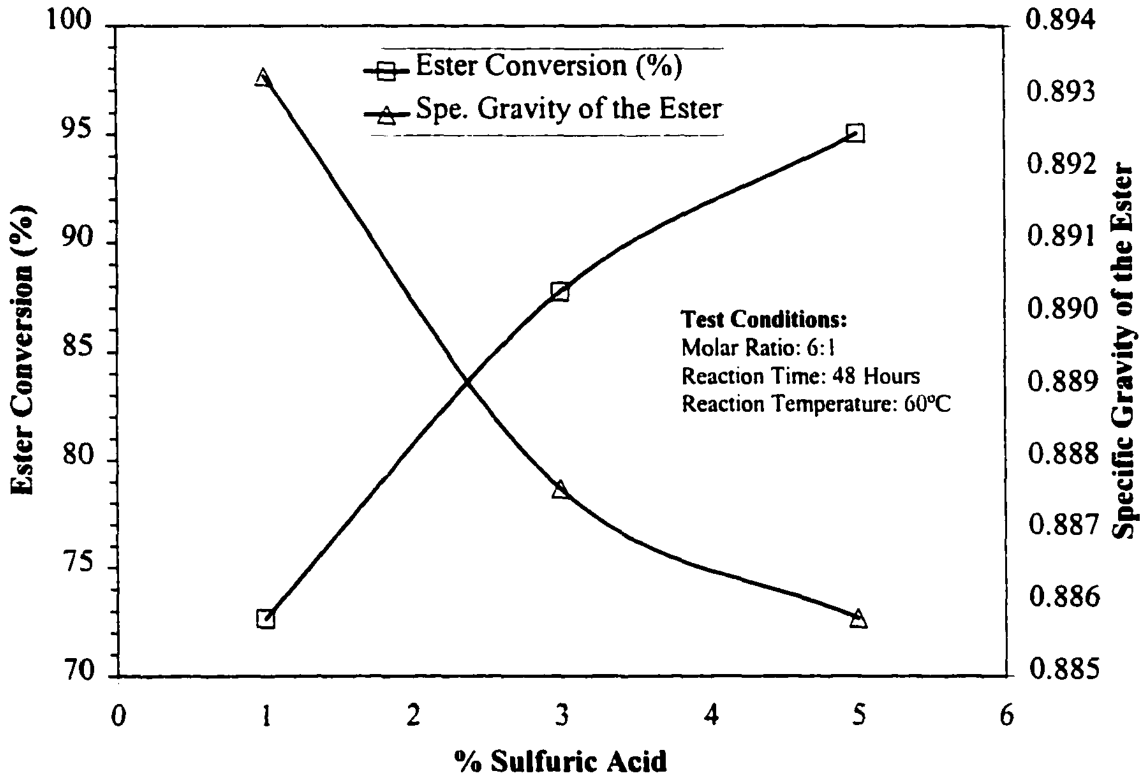


Figure 5.3: Effect of catalyst amount on ester conversion

5.1.4. Effect of Reaction Time

The reaction time was also expected to affect the conversion of vegetable oil to its ester. Two different reaction times, 48 and 96 hours, were evaluated. For each case, the reaction was conducted with 3% catalyst, 6:1 molar ratio, and a 60°C test condition. The relationship between reaction time and ester formation and specific gravity of methyl ester is shown in Table 5.5 and Figure 5.4. Ester formation increased with increasing reaction time. Ester conversions reached 87.8% and 95.1% at 48 hours and 96 hours, respectively. It should be noted that the same ester conversion that was achieved with 5% catalyst in 48 hours was measured with 3% catalyst after 96 hours.

Table 5.5: Effect of reaction time on ester conversion and specific gravity of ester

Run Time (hours)	*Ester Conversion (%)*	*Spe. Gravity of the Ester*
48	87.8	0.8876
96	95.1	0.8838

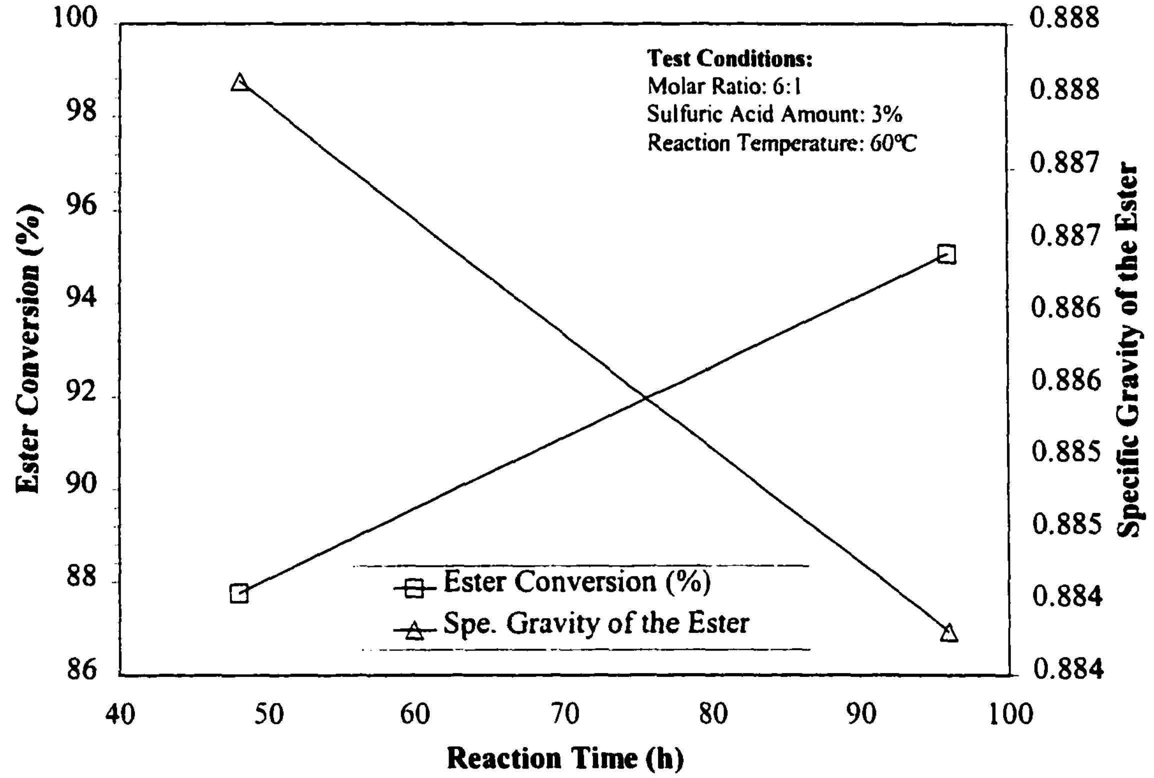


Figure 5.4: Effect of reaction time on ester conversion

5.1.5. Effect of Alcohol Type

To investigate the effect of different alcohol types on transesterification, 2-propanol, 1-butanol, ethanol, and methanol were tested for a 48-hour test period, with 3% sulfuric acid catalyst, and a 6:1 molar ratio of alcohol to oil. The reaction temperatures were selected to be a few degrees below the boiling points of the alcohols and are shown in Table 5.6. The relationship between alcohol type and ester conversion is also shown in Table 5.6. The highest ester conversion occurred with ethanol. The conversion to ethyl ester was 95.8% compared with 92.9%, 92.1%, and 87.8% for 2-propyl ester, 1-butyl ester, and methyl ester, respectively. The higher conversion rates found for the longer chain alcohols compared with methyl ester are probably due to the higher reaction temperatures allowed by their higher boiling points. This effect apparently dominates the decrease in reaction rate associated with longer chain alcohols noted by other researchers [38, 41].

Table 5.6: Effect of alcohol type on ester conversion and specific gravity of ester

Alcohol Type	*Boiling Temperature (°C)*	*Reaction Temperature (°C)*	*Ester Conversion (%)*	*Spec. Gravity of the Ester*
Methanol	65	60	87.8	0.8876
2-Propanol	82.4	75	92.9	0.8786
1-Butanol	117	110	92.1	0.8782
Ethanol	78.5	75	95.8	0.8814

5.1.6. Effect of Water

In the transesterification of vegetable oil with alkaline catalysts, it has been emphasized that the vegetable oil and alcohol should be water-free, since water strongly inhibits the reaction [47, 60].

To investigate the tolerance of water in acid-catalyzed transesterification, different amounts of distilled water were added to the vegetable oil. The test duration was 96 hours with 3% acid catalyst and the reaction was conducted at 60°C with a 6:1 molar ratio. The effect of the water percentage in the oil on the ester conversion and specific gravity of the methyl ester is shown in Table 5.7 and Figure 5.5. As little as 0.1% water addition (based on the weight of the vegetable oil) reduced the ester yield. When more water was added to the vegetable oil, the amount of methyl esters formed was significantly reduced. The addition of

5% water reduced the ester conversion to only 5.6% while the ester conversion without water was 95.1% at the same reaction conditions. Our results indicate that more than 0.5% water in the oil will decrease the ester conversion to below 92%.

Table 5.7: Effect of water on the ester conversion and specific gravity of the methyl ester

Water %	*Ester Conversion (%)*	*Spe. Gravity of the Ester*
0.0	95.1	0.8838
0.1	94.1	0.8875
0.3	94.0	0.8873
0.5	92.1	0.8873
1.0	83.6	0.8899
3.0	33.7	0.9102
5.0	5.6	0.9159

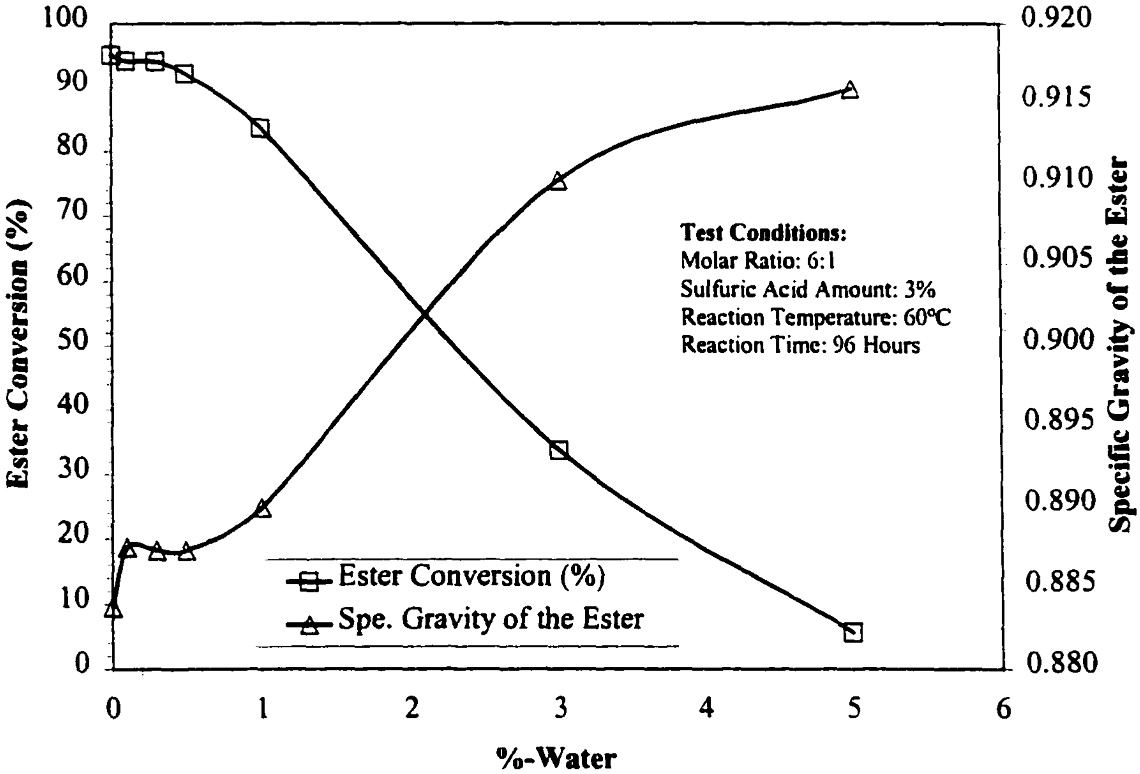


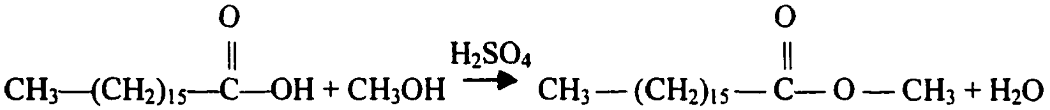
Figure 5.5: Effect of water on the ester conversion and specific gravity of the methyl ester

5.1.7. Effect of Free Fatty Acids

To investigate the effect of free fatty acid level on ester conversion, different amounts of palmitic acid (Aldrich Chemical Co., 99%) were added to soybean oil to obtain 5%, 10%, 15%, 20%, and 33% free fatty acid levels. Palmitic acid was chosen as a representative for the free fatty acids because it is easily obtained and relatively inexpensive. It also is one of the major fatty acids found in the processed grease from dead stock rendering plants, one of the feedstocks under consideration in the current study. The test conditions included a 96 hour test period, 3% sulfuric acid catalyst, 60°C, and 6:1 molar ratio. The relationship between the palmitic acid in the oil and the ester conversion and specific gravity of the methyl ester is shown in Table 5.8 and Figure 5.6.

The conversion rate of soybean oil to methyl ester drops below 90% for free fatty acid levels above 5%. An attempt was made to compare the tolerance of an alkaline catalyst (potassium hydroxide) to free fatty acids but the addition of 5% palmitic acid produced a solid soap mixture that prevented separation of the glycerin from the methyl ester.

The reaction of palmitic acid with methanol forms water as well as the ester, as shown in the reaction equation (5-1) below. As was seen in the previous section, water strongly inhibits the ester-formation reaction. For each case of palmitic acid addition, the water amount produced by the palmitic acid reaction was calculated, and compared with the water addition test. The results are shown in Figure 5.7. The test results show that the palmitic acid addition and the water addition tests have the same inhibiting effect on esterification. It appears that the inhibiting effect of the free fatty acids is entirely due to the water produced by the reaction. For comparison, the effect of water on an alkaline (KOH) catalyst is also shown. The results show that the transesterification with alkaline catalyst is more tolerant of water.



$$CH_3-(CH_2)_{15}-\overset{\overset{O}{\|}}{C}-OH + CH_3OH \xrightarrow{H_2SO_4} CH_3-(CH_2)_{15}-\overset{\overset{O}{\|}}{C}-O-CH_3 + H_2O \qquad (5\text{-}1)$$

Table 5.8: Effect of palmitic acid on the ester conversion and specific gravity of the methyl ester

% Palmitic Acid	*Ester Conversion (%)*	*Spe. Gravity of the Ester*
0	95.1	0.8838
5	90.5	0.8862
10	88.4	0.8866
15	80.3	0.8874
20	72.2	0.8887
33	58.8	0.8893

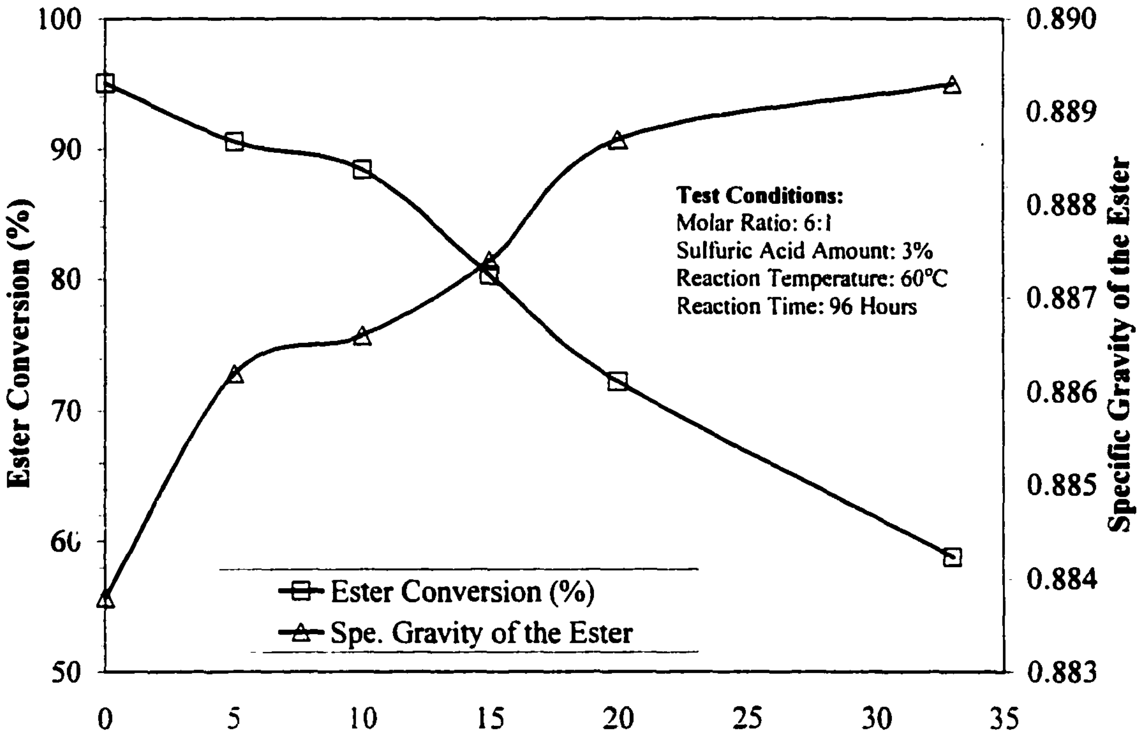


Figure 5.6: Effect of palmitic acid on the ester conversion and specific gravity of the methyl ester

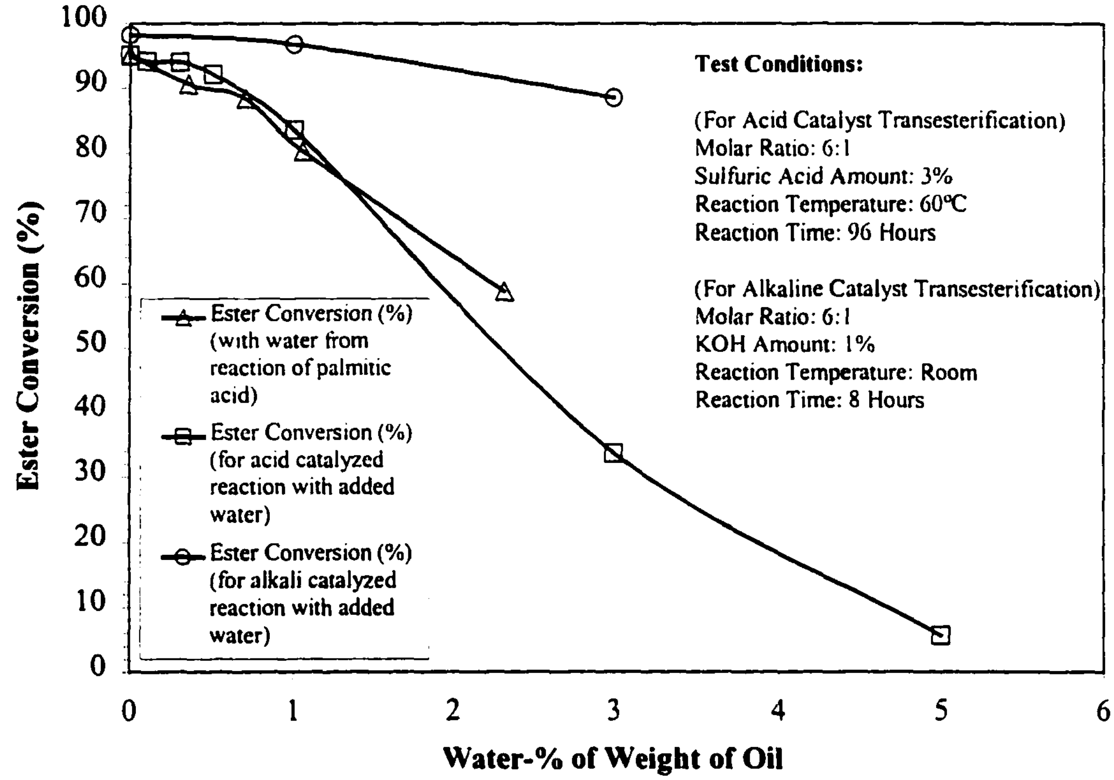


Figure 5.7: Comparison of the free fatty acid and water addition tests

5.1.8. Summary of the Acid Catalysis Study

The objective of this phase of the project was to investigate the acid-catalyzed methyl ester production process. The variables affecting ester formation including molar ratio, reaction temperature, catalyst amount, and reaction time were investigated to determine the best strategy for producing biodiesel. The following conclusions can be drawn from the acid-catalyzed biodiesel production study.

1. Acid-catalyzed transesterification is much slower than alkali-catalyzed transesterification.
2. The ester conversion efficiency is strongly affected by the molar ratio of alcohol to oil. In acid-catalyzed esterification, a higher molar ratio is required than for alkali-catalyzed.
3. If the acid-catalyzed reaction occurs at room temperature, the reaction is very slow and

poor ester conversion is obtained.

4. The completeness of ester formation increases with increasing acid catalyst amount.
5. The ester conversion is strongly inhibited by the presence of water in the oil. If the water concentration is greater than 0.5%, the ester conversion rate may drop below 90%.
6. Alcohols with high boiling temperature increase ester conversion. The higher reaction temperatures allowed by longer chain alcohols apparently dominate any tendency toward reduced reaction rates for these alcohols.
7. The amount of free fatty acids in vegetable oils can have a significant effect on the transesterification reaction. The water formed by the esterification inhibits further reaction. Free fatty acid levels above 5% can lower the ester conversion rate below 90%.

5.2. Preparation of Methyl Ester from Material with High FFA

The objective of this study was to prepare methyl esters from fats and oils with high FFAs. The work described in the previous section showed that it was possible to do this with acid catalysis. However, the reaction times were unacceptably long and water inhibition appeared to place a severe constraint on the FFA level that could be processed. Another researcher pointed out that the acid catalyzed reaction of the FFAs to monoesters was much faster than the reaction of triglycerides to monoesters [96]. This gave rise to the possibility of using an acid-catalyzed pretreatment step to convert the FFAs followed by an alkali-catalyzed step to convert the triglycerides. A search of the patent literature showed that others had taken advantage of this approach and some of this work was described in the literature review [63]. 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 our tests, a simulated animal fat was prepared to develop the procedure. Synthetic mixtures with high FFA were prepared by adding 20% and 40% palmitic acid 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 in the mixture, respectively. These are the initial values of acid value shown in the tables and figures presented below. As mentioned earlier, 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. The effects of molar ratio, reaction time, acid catalyst amount, and FFA level on the acid value of the mixture were determined at 60°C.

5.2.1. Process Development

The approach used in this study to convert the high FFA feedstock was to utilize acid catalysis to convert the FFAs to esters, a process that is relatively fast, and then to use alkaline catalysis to complete the process. Published results suggested that the acid catalysis must decrease the acid value of the mixture to less than 2 mg KOH/g and this was initial target for our pretreatment [23-25]. Previous work had shown that FFA levels above this amount result in less complete reaction and excessive soap formation. However, in work that will be presented later in this section, it was found that reducing the acid value to less than 1 mg KOH/g gives better results for some alkaline catalysts.

The decrease in the acid value of the mixture was monitored by periodically taking small samples from the reaction vessel. After the samples were stored in a refrigerator, their acid values were measured using the American Oil Chemists' Society (A.O.C.S.) Official

Method Cd 3a-63 for Acid Value [97]. The test procedure is given in Appendix B. The effect of the acid catalyst amount, reaction time, FFA level, and alcohol type on the acid value of the mixture was determined at 60°C and 6:1 molar ratio. The sulfuric acid and methanol amounts were calculated in this section based on the total weight of the oil/FFA mixture.

5.2.1.1. 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% palmitic acid, four different catalyst amounts (0, 1, 3, and 5%) and a 1 hour reaction time were selected. The percentage of the catalyst referred to here is based on a fraction of the total weight of oil and FFA present. After the initial mixing of the reactants, samples were extracted at 1 minute, 15 minutes, 30 minutes, and 60 minutes. The acid values of the original vegetable oil and the vegetable oil/palmitic acid mixture before the alcohol was added were also recorded. All samples from the test with zero catalyst were solid at room temperature and required heating to allow measurement of the acid value. After 1 hour, the reacting mixture was allowed to settle. An alcohol-water mixture was collected at the top of the separatory funnel for the 1% catalyst amount test. However, for the 3 and 5% catalyst tests the alcohol-water mixture collected at the bottom of the funnel.

At 6:1 molar ratio, the influence of the catalyst amount on the acid value during the one-hour test, is shown in Table 5.9 and plotted in Figure 5.8. As can be seen, with zero catalyst the acid value reached only 33.38 mg KOH/g at the end of the test. However, there is a very rapid reduction in acid value that occurs immediately after addition of the alcohol-acid catalyst solution to the oil-FFA mixture. With the addition of 1% catalyst, the lowest acid value measured after 1 hour was 1.77 mg KOH/g. With the addition of 3% and 5%

catalyst, the lowest acid values measured were 0.67 mg KOH/g and 0.54 mg KOH/g at the end of the test, respectively. After the catalyst solution addition, the acid values of the mixtures were measured to be almost the same.

Table 5.9: Effect of catalyst amount and reaction time on the acid value for 20% palmitic acid in the mixture

Run Time (hours)	***A.V. (mg KOH/g) at 0% Cat.***	***A.V. (mg KOH/g) at 1% Cat.***	***A.V. (mg KOH/g) at 3% Cat.***	***A.V. (mg KOH/g) at 5% Cat.***
Soybean Oil	0.10	0.10	0.10	0.10
After Palmitic Acid Addition	41.33	41.33	41.33	41.33
After Solution Addition	38.19	13.66	13.44	14.45
0.25	37.07	5.80	2.86	4.30
0.50	35.73	3.83	1.15	0.92
1.00	33.38	1.77	0.67	0.54

5.2.1.2. Effect of FFA Level

To investigate the effect of FFA level, the palmitic acid amount in the mixture was increased to 40%. Three different catalyst amounts (1, 3, and 5%) and a 1-hour reaction time were selected at 6:1 molar ratio of methanol to oil. The sampling procedure was the same as was used for the tests with 20% palmitic acid.

After 1 hour, the reacting mixture was allowed to settle. For the 1% catalyst amount test, the alcohol-water mixture was collected at the top of the separatory funnel, but for the 3% and 5% catalyst tests the alcohol-water mixture collected at the bottom of the funnel due to higher water formation during the reaction for these two catalyst levels.

The influence of the catalyst amount on the acid value for 40% palmitic acid addition is shown in Table 5.10 and plotted in Figure 5.9. When the FFA level was increased to 40%,

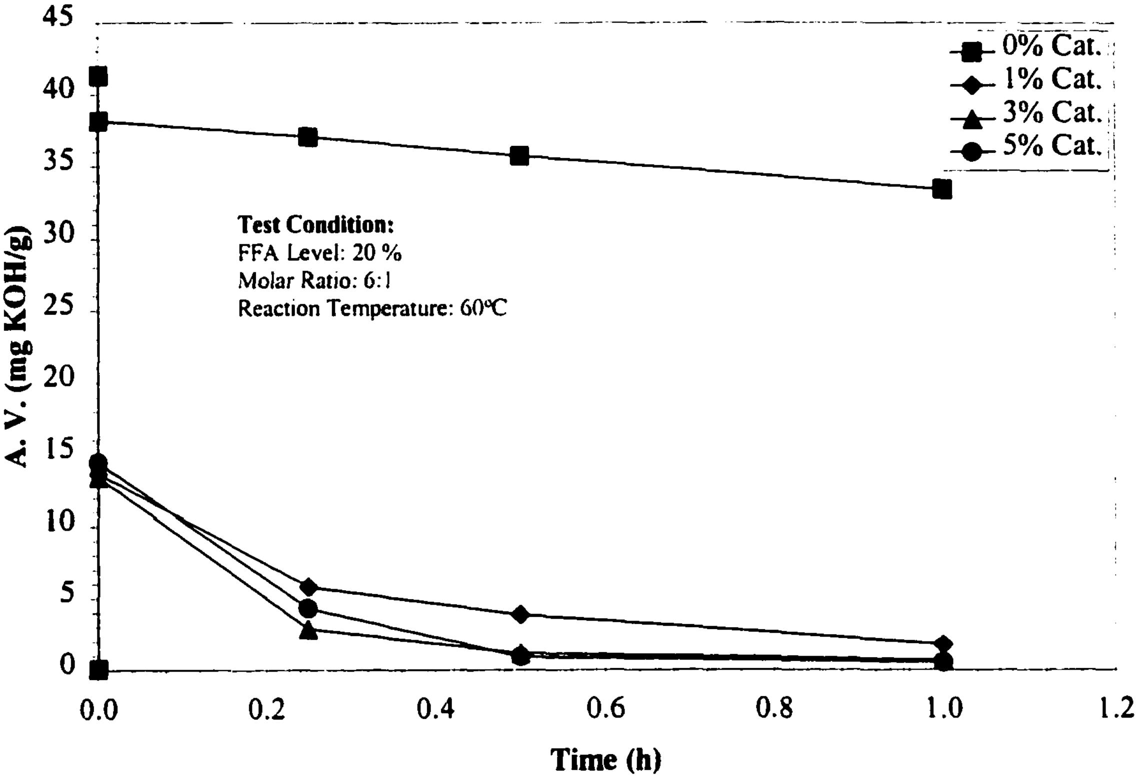


Figure 5.8: Effect of catalyst amount and reaction time on the acid value for 20% palmitic acid in the mixture

Table 5.10: Effect of catalyst amount and reaction time on the acid value for 40% palmitic acid in the mixture

Run Time (hours)	***A.V. (mg KOH/g) at 1% Cat.***	***A.V. (mg KOH/g) at 3% Cat.***	***A.V. (mg KOH/g) at 5% Cat.***
Soybean Oil	0.10	0.10	0.10
After Palmitic Acid Addition	91.73	91.73	91.73
After Solution Addition	27.89	23.52	37.52
0.25	22.40	19.15	21.06
0.50	21.84	14.11	13.17
1.00	18.82	8.09	6.25

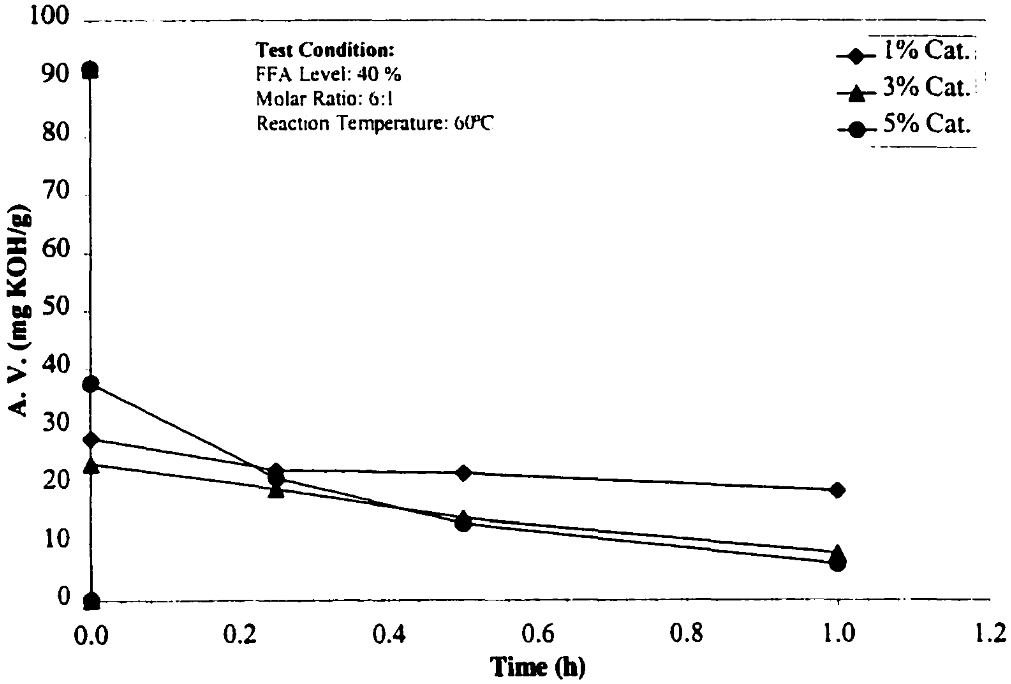


Figure 5.9: Effect of catalyst amount and reaction time on the acid value for 40% palmitic acid in the mixture

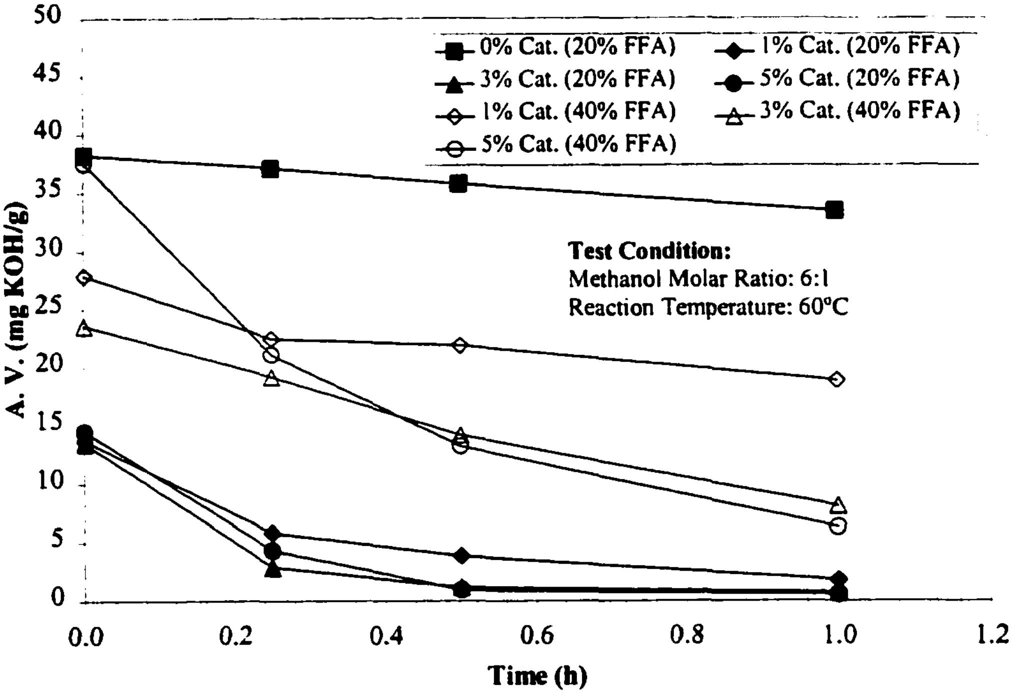


Figure 5.10: Comparison of the acid values of 20% and 40% palmitic acid test

the initial acid value was measured to be 91.73 mg KOH/g. At the three catalyst levels studied, 1%, 3%, and 5%, the acid values measured after 1 hour were 18.82, 8.09, and 6.25 mg KOH/g, respectively. The 20% and 40% palmitic acid tests are compared in Figure 5.10. The final acid value of the 40% palmitic acid test did not get as low as the 20% palmitic acid test due to water formation.

5.2.1.3. Effect of Alcohol Type

To investigate the effect of different alcohol types 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 molar ratio was 6:1 and the catalyst amounts were 1, 3, and 5 %, based on the total mixture weight, for a 1-hour reaction time. Samples were extracted at the same times as the earlier tests. The test results are shown in Table 5.11 and plotted in Figure 5.11 for the 20% palmitic acid addition case. The minimum acid value, after 1-hour, was measured to be 3.00 mg KOH/g with 5% sulfuric acid. The acid values of the 1% and 3% catalyst test were 3.79 mg KOH/g and 3.50 mg KOH/g, respectively, at the end of the test. It is clear from Figure 5.11 that most of the reaction with ethanol occurs very quickly and very little additional reaction occurs after 15 minutes.

The test results for the 40% palmitic acid addition case with ethanol are shown in Table 5.12 and plotted in Figure 5.12. After the 1 hour reaction, the minimum acid values were measured to be 8.09, 5.60, and 6.45 mg KOH/g for 1, 3, and 5% catalyst, respectively. As with the 20% palmitic acid case, the acid values of the samples after the initial ethanol addition did not change much, giving almost a flat line. This indicates that the ethanol reacts more quickly than methanol. Another observation was that the samples taken in the tests with ethanol did not freeze while being stored in the refrigerator.

5.2.2. Development of 2-Step Pretreatment Process

The approach used in this study to process high FFA feedstocks was to use acid catalysis to convert the FFAs to esters, a process that is relatively fast, and then to use alkaline catalysis to complete the process. In the literature [23-25], it has been mentioned that the oil should not contain more than 1% FFA for alkaline transesterification reactions. This corresponds to an acid value of 2 mg KOH/g. If the FFA level exceeds this amount, the

Table 5.11: Effect of ethanol on acid value for 20% palmitic acid test

Run Time (hours)	*A.V. (mg KOH/g) at 1% Cat.*	*A.V. (mg KOH/g) at 3% Cat.*	*A.V. (mg KOH/g) at 5% Cat.*
Soybean Oil	0.10	0.10	0.10
After Palmitic Acid Addition	41.33	41.33	41.33
After Solution Addition	4.14	4.19	3.35
0.25	4.17	3.58	2.46
0.50	3.79	3.50	2.73
1.00	3.63	3.57	3.00

Table 5.12: Effect of ethanol on acid value for 40% palmitic acid test

Run Time (hours)	*A.V. (mg KOH/g) at 1% Cat.*	*A.V. (mg KOH/g) at 3% Cat.*	*A.V. (mg KOH/g) at 5% Cat.*
Soybean Oil	0.10	0.10	0.10
After Palmitic Acid Addition	91.73	91.73	91.73
After Solution Addition	8.96	6.92	7.80
0.25	9.18	7.15	5.35
0.50	8.89	5.49	6.61
1.00	8.09	5.60	6.45

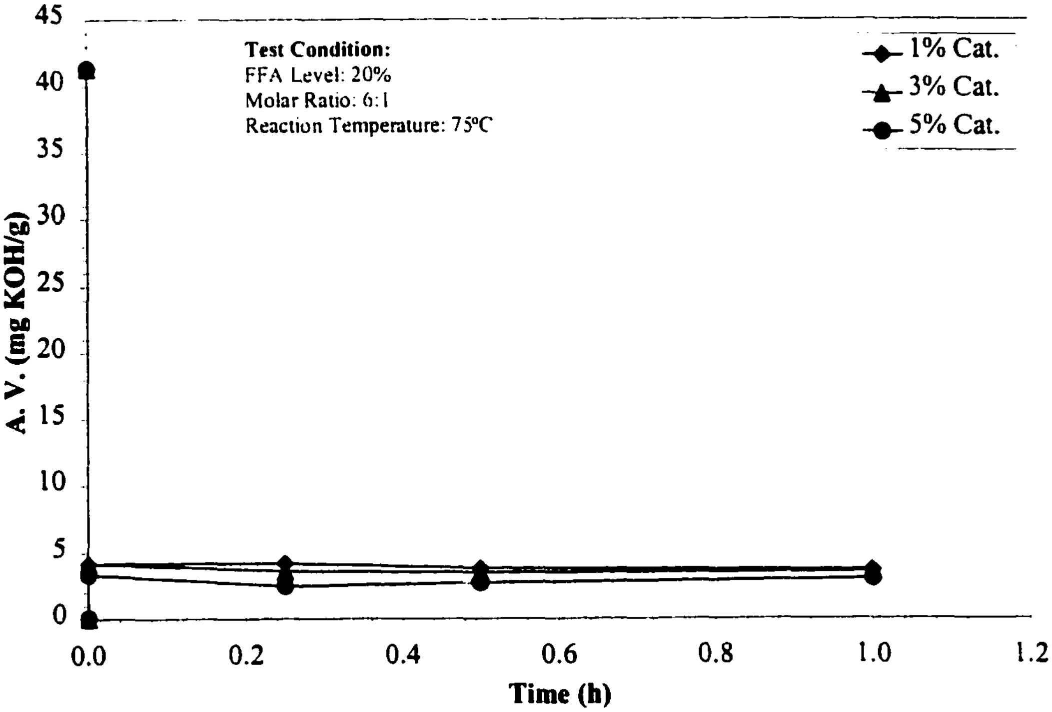


Figure 5.11: Effect of ethanol on acid value for 20% palmitic acid test

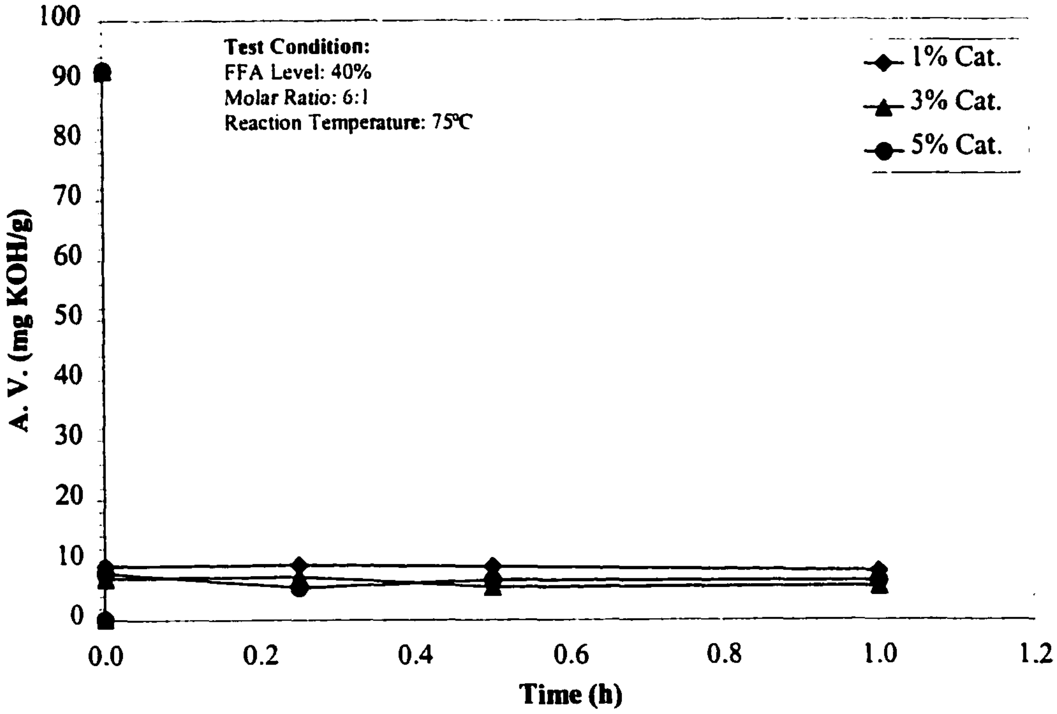


Figure 5.12: Effect of ethanol on acid value for 40% palmitic acid test

formation of soap will prevent 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 0.5% FFA for at least one alkaline catalyst, and this is supported by other researchers [44, 61]. 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. It will be shown that this can be accomplished with a 2-step process. When alcohol reacts with the FFA in the acid-catalyzed esterification process, water is formed. As mentioned earlier, the presence of water in the transesterification reaction greatly decreases the ester conversion. Therefore, the water produced in the mixture must be removed before the reaction will continue. This can be accomplished by adding alcohol and acid to the high FFA feedstock as a first step. Then after stirring for an hour at 60°C, the mixture is allowed to settle and an alcohol-water fraction rises to the top. This alcohol-water fraction can be removed and additional alcohol and acid added as a second step.

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. The general procedure for this 2-step reaction was as follows. After the palmitic acid was melted and mixed with the soybean oil at 60°C, the solution of sulfuric acid in methanol was added while stirring. The sulfuric acid and methanol amounts were based on the FFA level in the mixture. This is a different procedure than was used for the experiments described in the previous sections. Since the alcohol and catalyst are only reacting with the FFAs it seemed more logical to base the amounts of the reactants on the FFAs instead of the total amount of oil-FFA mixture. After the required reaction time, the mixture was allowed to settle in a separatory funnel overnight. Then, the oil and ester mixture was separated from the water and excess alcohol which were present together as a separate phase. After measuring the new acid value of the oil and ester mixture, it was reheated to 60°C and a second batch of sulfuric acid in methanol was added. This time, the sulfuric acid and methanol amounts were based on the FFA level remaining in the mixture after the first step. Again, after the reaction time was complete, the mixture settled overnight and the excess alcohol and water were removed.

After determining the best strategy for reducing the acid value of the mixture to less than 2 mg KOH/g, the reaction process was continued with alkaline-catalyzed transesterification. In this step, the amounts of alcohol and alkaline catalyst were based on the fraction of unreacted oil in the mixture. The variables affecting the completeness of the reaction were then determined for the alkaline catalyst transesterification. After this third step was completed, the ester was separated from the glycerin in a separatory funnel and washed to remove the soap and catalyst in the mixture. Then, about 50 ml of glycerin were added to the ester to remove the mono- and diglycerides and then the ester was washed with water two more times to remove any residual free glycerin. Finally, the completeness of the reaction was measured using the total remaining glycerin as described earlier.

5.2.2.1. Effect of Molar Ratio, Catalyst Amount, and Reaction Time in First Step

The molar ratio of alcohol to FFA is one of the most important factors that influences the reduction of the acid value of the mixture. For the stoichiometric reaction, 1 mole of alcohol is required per mole of FFA to convert the FFA to ester. In reality, the molar ratio should be higher than the theoretical ratio to drive the reaction to completion. To investigate the effect of molar ratio, three different molar ratios, 6:1, 8:1, and 10:1, were selected. To understand the effect of catalyst amount, four different catalyst amounts, 3%, 5%, 10%, and

15%, were selected. In the calculation of molar ratio and catalyst amount, the weight of FFA in the mixture was taken as the base for the catalyst percentages. Each reaction was run for 30 minutes at 60°C. The changes in the acid value of the mixture for the first step reaction are shown in Table 5.13 and Figure 5.13. As seen in the table and figure, the FFA level in the oil was strongly affected by the molar ratio of alcohol to oil. A higher molar ratio gave a much larger decrease in the acid value of the feedstock. If a lower molar ratio is used, much more time was required to reach an acceptable FFA level of the feedstock. The acid catalyst amount was also very effective in decreasing the acid value of the mixture.

To understand the effect of reaction time, the acid value was measured at four different times, 0.25, 0.50, 0.75, and 1.00 hours, for a 5% catalyst amount at 60°C. The changes in the acid value of the mixture are shown in Table 5.14 and Figure 5.14. The acid value for this case of 20% FFA was actually reduced to less than 2 mg KOH/g after 1 hour with the 10:1 molar ratio of methanol to FFA. While these data indicated that it was possible to reduce the FFA level the required amount with a single pretreatment step, it was decided that a lower molar ratio of alcohol and shorter time would be more cost effective so a second pretreatment step was investigated.

5.2.2.2. Effect of Molar Ratio, and Reaction Time in Second Step

To investigate the effect of the molar ratio on the second step reaction, three mixtures were prepared with a 20% palmitic acid solution in soybean oil that had been reacted with 5% sulfuric acid solution in 6:1, 8:1, and 10:1 molar ratios for the first step reaction. The first step reaction time was selected to be 30 minutes. After settling in the separatory funnel, the alcohol-water mixture was removed and the acid values of the remaining parts were

Table 5.13: Effect of catalyst amount on acid value of the synthetic mixture at different molar ratio and 30 minutes reaction time

Catalyst	*A.V. (mg KOH/g) at 6:1 Molar Ratio*	*A.V. (mg KOH/g) at 8:1 Molar Ratio*	*A.V. (mg KOH/g) at 10:1 Molar Ratio*
Soybean Oil	0.10	0.10	0.10
After Palmitic Acid Addition	41.33	41.33	41.33
3% H_2SO_4	14.49	11.54	7.15
5% H_2SO_4	11.54	8.31	5.76
10% H_2SO_4	6.34	3.92	2.40
15% H_2SO_4	6.56	4.28	1.37

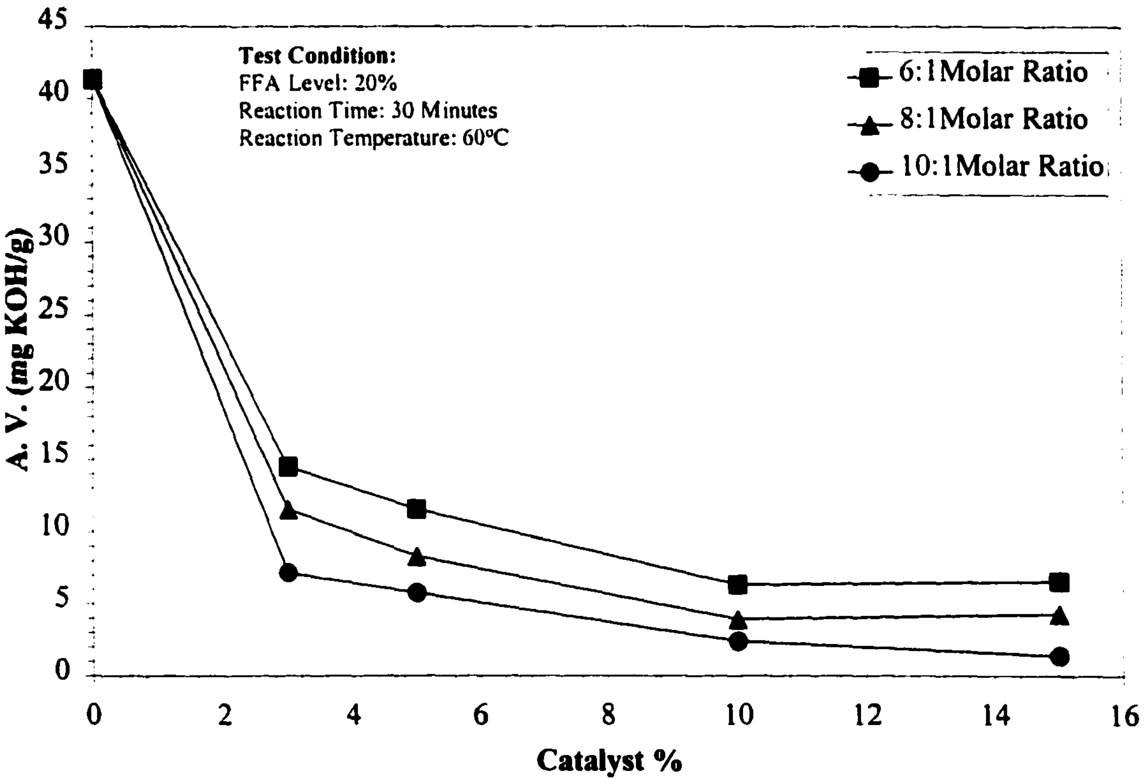


Figure 5.13: Effect of catalyst amount on acid value of the synthetic mixture

Table 5.14: Effect of reaction time on acid value of the synthetic mixture at different molar ratio and 5% catalyst amount

Reaction Time (hours)	*A.V. (mg KOH/g) at 6:1 Molar Ratio*	*A.V. (mg KOH/g) at 8:1 Molar Ratio*	*A.V. (mg KOH/g) at 10:1 Molar Ratio*
Soybean Oil	0.10	0.10	0.10
After Palmitic Acid Addition	41.33	41.33	41.33
0.25	14.45	11.49	7.68
0.50	11.54	8.31	5.76
0.75	10.10	5.80	3.02
1.00	8.85	4.10	1.95

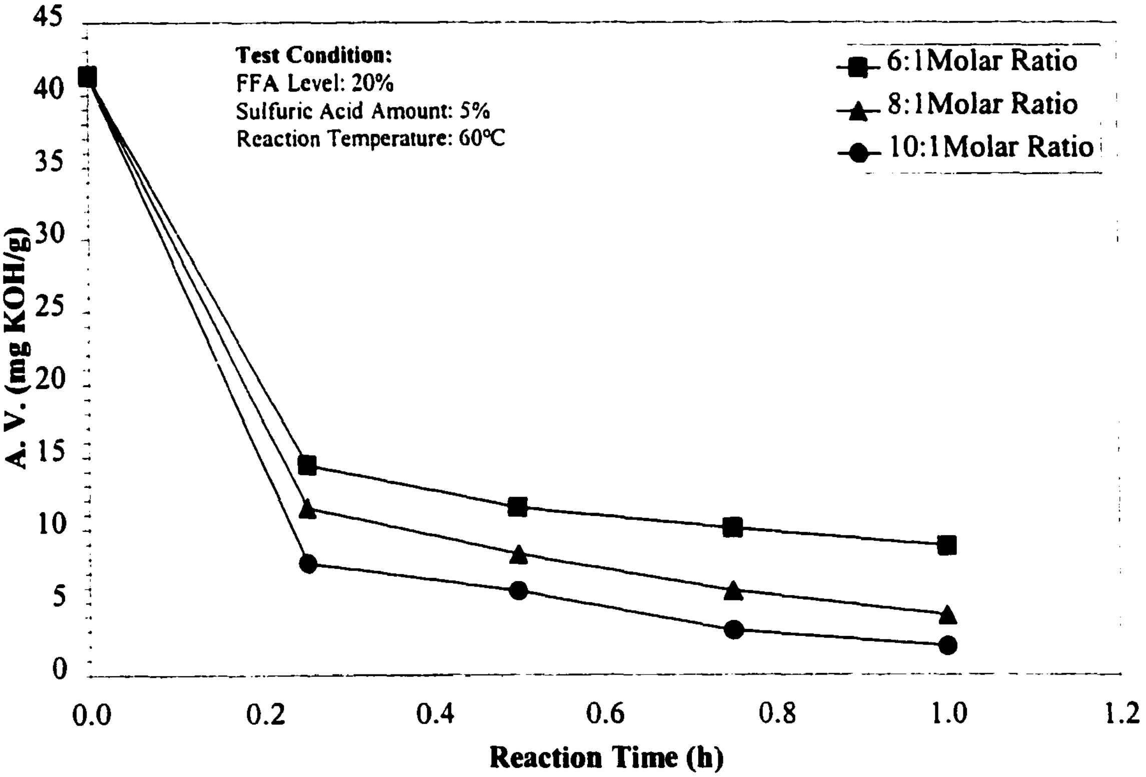


Figure 5.14: Effect of reaction time on acid value of the synthetic mixture

measured. The acid values of the mixtures for the 6:1, 8:1, and 10:1 molar ratios were 11.94, 8.58, and 6.34 mg KOH/g, respectively, at the end of the first step. These values are very close to the values given in Table 5.14. Then, these samples were used in the second step reaction to investigate the effect of the second step molar ratio. In the second step reaction, the sulfuric acid and methanol amount were based on the FFA level remaining in the mixture after the first step. For each test, the molar ratio was varied up to 15:1 to reduce the acid value of the oil mixture to less than 2 mg KOH/g. The changes in the acid value of the mixture are shown in Table 5.15 and plotted in Figure 5.15. As stated in the previous section, the FFA level in the oil was strongly affected by the molar ratio of alcohol to oil and the reaction time. However, it was noted that only one case had achieved the 2 mg KOH/g target and it required what was believed to be an excessive amount of methanol. To conserve methanol, longer reaction times for the pretreatment steps were investigated.

When the reaction time was extended to 1 hour at the first step for the 10:1 molar ratio, the acid value of the mixture decreased to 2.87 mg KOH/g as shown in Table 5.16. Using samples from this first step, the reaction time was also extended to 1 hour in the second step and the second step molar ratio was varied from 6:1 to 35:1. This time, the acid value of the mixture decreased to less than 2 mg KOH/g even with the 6:1 molar ratio in the second step as can be seen in Table 5.17 and Figure 5.16. 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.

Table 5.15: Effect of molar ratio in second step for 30 minutes reaction time

Methanol Molar Ratio	*A.V. (mg KOH/g) after 6:1Molar Ratio in 1st Step Reaction*	*A.V. (mg KOH/g) after 8:1Molar Ratio in 1st Step Reaction*	*A.V. (mg KOH/g) after 10:1Molar Ratio in 1st Step Reaction*
Before 2nd Step	11.94	8.58	6.34
2nd Step Molar Ratio 2:1	6.34	-	-
2nd Step Molar Ratio 4:1	5.67	-	-
2nd Step Molar Ratio 6:1	5.44	3.65	2.76
2nd Step Molar Ratio 8:1	5.04	3.20	2.35
2nd Step Molar Ratio 10:1	-	2.76	2.31
2nd Step Molar Ratio 15:1	2.98	2.31	1.86

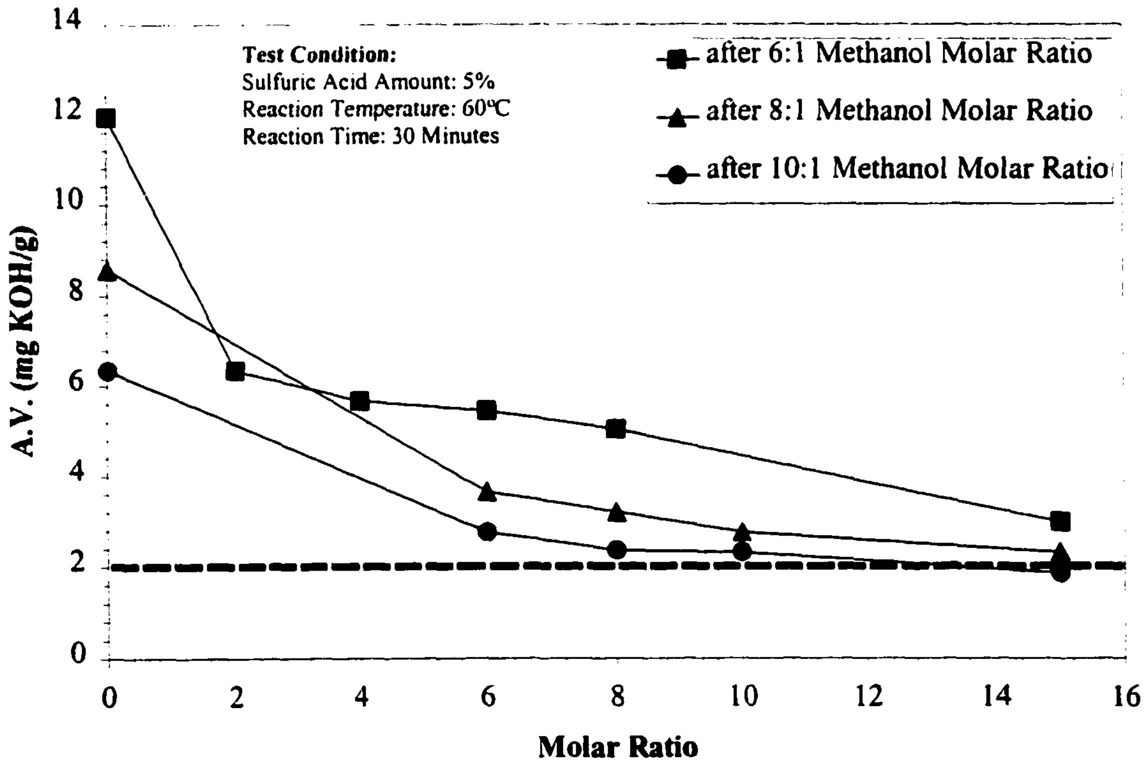


Figure 5.15: Effect of molar ratio in second step for 30 minutes reaction time

Table 5.16: Effect of reaction time on the acid value of the mixture in 1st step

Reaction Time (hours)	*A.V. (mg KOH/g) at 10:1 Molar Ratio*
0.50	6.34
1.00	2.87

Table 5.17: Effect of molar ratio on the acid value of the mixture in 2nd step for 1 hour reaction

Methanol Molar Ratio in 2nd Step	*A.V. (mg KOH/g) after 10:1 Molar Ratio*
Before 2nd Step	2.87
6:1	1.64
8:1	1.55
10:1	1.41
15:1	1.19
20:1	0.96
25:1	0.87
30:1	0.74
35:1	0.52

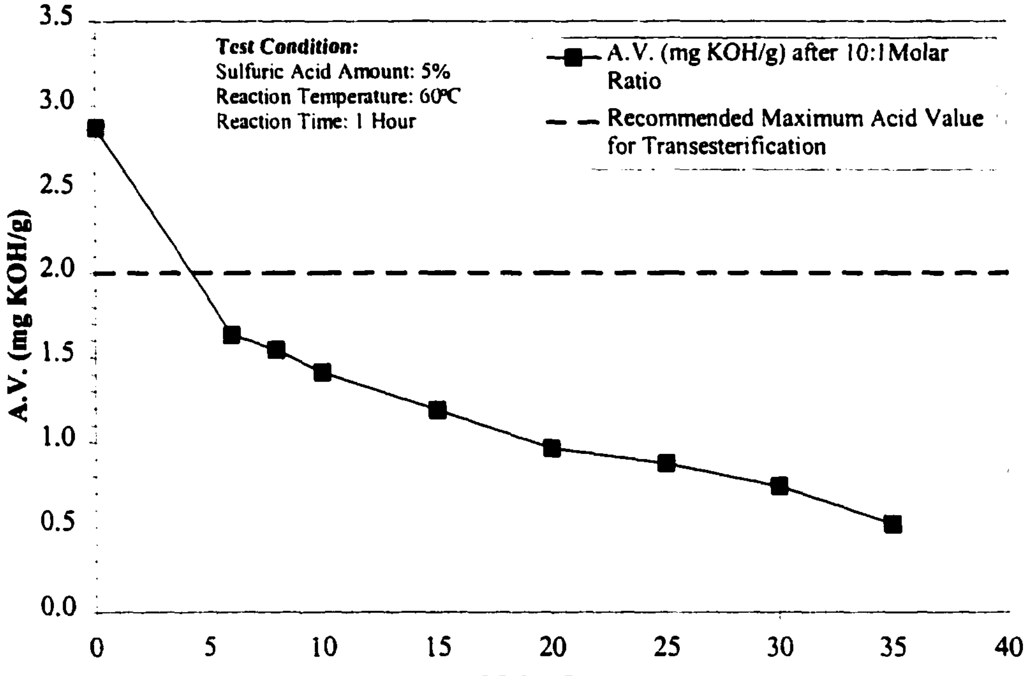


Figure 5.16: Effect of molar ratio on the acid value of the mixture in 2nd step for 1 hour reaction

5.2.2.3. 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 in the 2-step reaction, the reaction process was continued with alkaline-catalyzed transesterification. In this process, the amounts of alcohol and alkaline catalyst were based on the amount of unreacted oil in the mixture. An alkaline-catalyzed transesterification reaction was run using the sample which had the initial acid value of 1.86 mg KOH/g with a 6:1 molar ratio of methanol and 1% alkaline catalyst (KOH). However, the total glycerin amount was measured to be 0.29%. This total glycerin amount was too high to meet the total glycerin amount specification. Therefore, five other samples with initial acid values ranging from 1.19 to 0.52 mg KOH/g were subjected to the alkaline-catalyzed transesterification reaction. A 6:1 molar ratio of methanol and 1% alkaline catalyst (KOH) were used. An additional amount of KOH was added to neutralize the residual FFA in the oil mixture. The reaction continued at room temperature for 8 hours. After this third step was completed, the ester was separated from the glycerin in a separatory funnel and water washed to remove the soap and catalyst in the mixture. Then, glycerin was added to the ester and stirred to extract mono- and diglycerides from the ester and the ester was water washed two more times to remove residual glycerin in the ester. Finally, the completeness of the reaction was measured using A.O.C.S Official method Ca 14-56. The total glycerin measured in the ester and the specific gravity of the ester are shown in Table 5.18 and plotted in Figure 5.17. The yield shown in Table 5.18 was calculated by dividing the final weight of ester by the weight of oil/FFA mixture at the beginning.

The American Society for Testing and Materials is currently considering a standard for biodiesel that would require the total glycerin to be less than 0.24%. Our study showed that to produce ester which met this total glycerin requirement, the initial acid value of the oil should be 1 mg KOH/g (0.5% FFA) or less for a 6:1 molar ratio of methanol and 1% KOH catalyst. Using more KOH catalyst or a higher molar ratio of methanol could potentially reduce the total glycerin or make the reaction more tolerant of FFAs. References [37, 44] confirm our results. Results to be reported later show that another catalyst, sodium methoxide, is more tolerant of FFAs than KOH.

Table 5.18: Effect of acid value on total glycerin and specific gravity

A.V. (mg KOH/g)	*Total Glycerol (%)*	*Spe. Gravity*	*Yield (%)*
1.19	0.25	0.8767	90.76
0.96	0.23	0.8758	89.63
0.87	0.23	0.8757	90.23
0.74	0.22	0.8758	87.78
0.52	0.22	0.8758	88.20

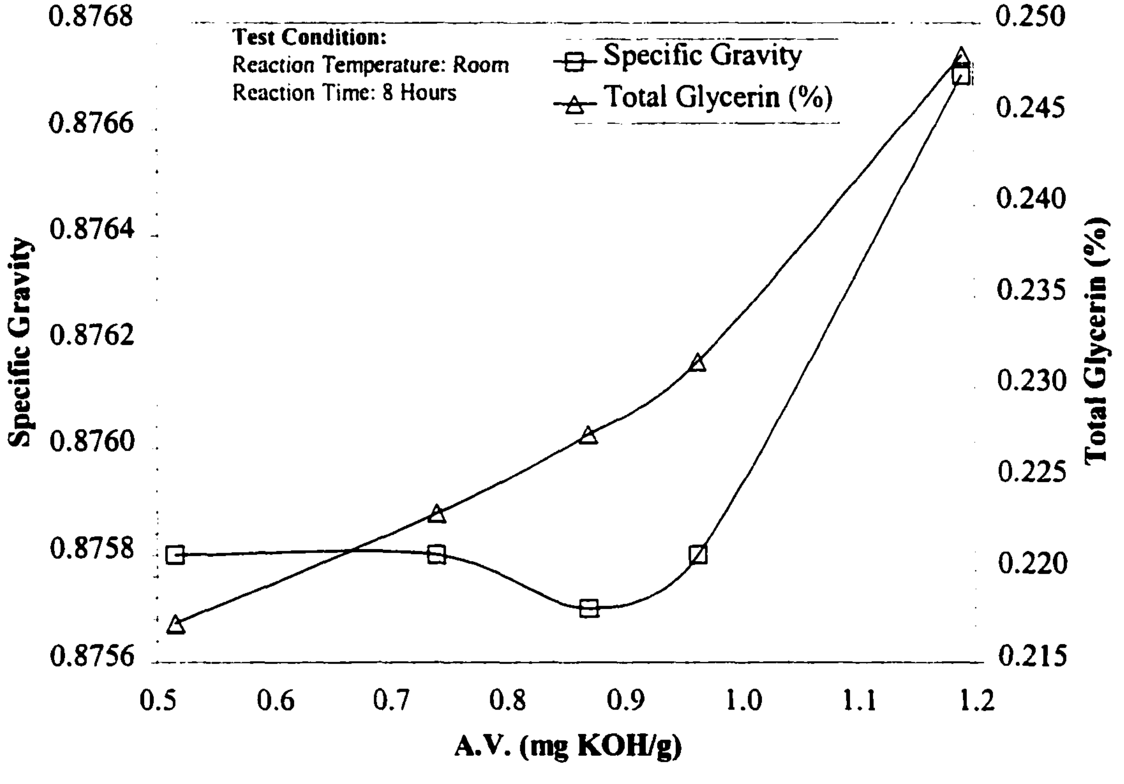


Figure 5.17: Effect of acid value on total glycerin and specific gravity

5.2.3. Summary of the Preparation of Methyl Ester from Material with High FFA

One of the objectives of this project was to reduce the FFA level of the feedstock to less than 1% (acid value = 2 mg KOH/g) using an acid catalyst. However, when alcohol reacts with the FFAs in the acid-catalyzed esterification process, water is formed and inhibits the reaction. Therefore, the water produced in the mixture must be removed before the reaction will continue. The approach developed in this study to convert a high FFA feedstock was to use acid catalysis to convert the FFAs to esters, a process that is relatively fast. Then the water is removed with the alcohol when the mixture is allowed to separate. Additional alcohol and acid catalyst can then be added to continue the process. Elimination of the FFA may require multiple steps. Then, additional alcohol and alkaline catalyst are added to complete the process.

The following conclusions can be drawn from this portion of the study of transesterification using synthetic mixtures with high FFAs.

1. Current work indicates that the acid catalysis can decrease the acid value of the synthetic mixture to less than 2 mg KOH/g with a 2-step process.
2. Using the 2-step acid-catalyzed pretreatment followed by an alkali-catalyzed final reaction, the transesterification reaction may be completed in much less time compared with acid-catalyzed transesterification alone.
3. The FFA level of the feedstock is strongly affected by the molar ratio of alcohol to oil. In acid-catalyzed esterification, a higher molar ratio is required to decrease the acid value of the feedstock. If a lower molar ratio is used, the FFA level of the feedstock requires much more time to reach acceptable levels.

4. Increasing the acid catalyst amount is very effective in decreasing the acid value of the mixture. In the first step, at a 10:1 molar ratio for a 30 minutes reaction time, the acid value of the mixture with 20% palmitic acid was reduced to 1.37 mg KOH/g and 7.15 mg KOH/g for 15% and 3% acid catalyst, respectively. The FFA level may be reduced using no catalyst but long times are required.
5. Ethanol, which has a higher boiling temperature than methanol, decreased the FFA level of the synthetic mixture faster than methanol. The higher reaction temperatures may be the reason for this difference.
6. With KOH as the alkaline catalyst, it was found that 1 mg KOH/g (0.5% FFA) was a better target for acid value reduction. After decreasing the acid value of the feedstock to less than 0.5% FFA level, the alkaline-catalyzed transesterification gives good ester conversion. The biodiesel produced met the total glycerin specification.

5.3. Preparation of Methyl Esters from Yellow Grease

The next task of this study was to prepare methyl esters from actual yellow grease to validate the methods developed using the simulated high FFA feedstock. The yellow grease was obtained from the Simonsen rendering plant in Quimby, Iowa. The first step in processing this material was to filter out the insoluble materials (such as meat and bone particles) at around 55°C or 60°C. Then, the two step acid-catalyzed reaction described earlier was applied to the feedstock to reduce its acid value to less than 2 mg KOH/g. Rendering plant feedstock typically has an initial FFA level between 5 and 25% FFA. The specific fat analyzed for this project had an acid value of 25.15 mg KOH/g which corresponds to FFA level of about 12%. The fatty acid distribution of the yellow grease is shown in Table 5.19. For the yellow grease used, the saturated palmitic and stearic acid amounts were 21.75% and 12.05%, respectively. The large amount of saturated fat implies that the fat is more stable against oxidation than an unsaturated oil such as soybean oil and more saturated oils and fats produce higher cetane number fuel. However, this high fraction of saturated fat also means that the fat was solid at room temperature.

The esterification process was repeated for different alcohol molar ratios, amounts of acid catalyst, and reaction times at 60°C. After the acid value was reduced to less than 2 mg KOH/g, the transesterification reaction was continued with the alkaline catalyst at room temperature for 8 hours. The completeness of the reaction was measured using A.O.C.S Official method Ca 14-56 as before. The following sections provide the results of these tests with yellow grease.

Table 5.19: Fatty acid composition of the yellow grease and soybean oil

Product	Carbon Chain (%)*										***Unknown***	***Sat.***
	C14:0	***C15:0***	***C16:0***	***C16:1***	***C17:0***	***C18:0***	***C18:1***	***C18:2***	***C18:3***	***C20:0***	***Components***	***(%)***
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

*Measured by Woodson-Tenent Laboratories, Inc., Des Moines, IA.

5.3.1. Effect of Molar Ratio and Reaction Time on the Acid Value of Yellow Grease in First Step and Second Step

After filtering the yellow grease at 55-60°C, a 5% sulfuric acid solution with an 8:1 molar ratio of methanol, based on the FFA level, was added. In the calculations, the molecular weight of FFA was assumed to be the same as the molecular weight of palmitic acid. The reaction was continued for 30 minutes at 60°C. After settling overnight and separating the alcohol-water mixture on 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 and was too high for the reaction to be continued for the second step. Therefore, the first step was repeated with the molar ratio increased to 20:1 and the reaction time increased to 1 hour. At this time, the acid value of the oil mixture was measured to be 5.22 mg KOH/g after the first step reaction as seen in Table 5.20.

After obtaining an acceptable acid value in the first step with a 20:1 molar ratio, 5% sulfuric acid, and 1-hour reaction time, the reaction was continued for the second step at three different molar ratios with 5% sulfuric acid for 1 hour. The changes in the acid value of the mixture are shown in Table 5.21. When the molar ratio was increased, the acid value of

Table 5.20: Effect of molar ratio and reaction time on acid value in first step and comparison with synthetic mixture

Methanol Molar Ratio	*Reaction Time (hours)*	*A.V. for Yellow Grease (mg KOH/g)*	*A.V. for Synthetic Mixture (20% Palmitic Acid) (mg KOH/g)*
Before Test	-	25.15	41.33
8:1	0.5	14.63	8.31
20:1	1.0	5.22	-

Table 5.21: Effect of molar ratio on acid value in second step at 5% catalyst amount

Methanol Molar Ratio	*Reaction Time (hours)*	*A.V. (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

the mixture decreased to as low as 0.74 mg KOH/g with a 40:1 molar ratio of methanol to FFA. These methanol amounts for the first and second steps are much greater than was expected based on the preliminary work with the synthetic high FFA feedstock. As shown in Table 5.20, 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 8:1 molar ratio while the yellow grease which started at 25.15 mg KOH/g only decreased to 14.63 mg KOH/g.

The difference in the effectiveness of the acid catalyst between the synthetic mixture and the yellow grease was unexpected. A number of possible reasons for the difference were proposed. Animal fat contains some moisture, as well as unknown, insoluble, and unsaponifiable material equal to between 1% and 2% of its weight. These compounds may effect the reaction results. Initially it was thought that the water in the fat could be inhibiting the reaction. However, in the feedstock with 12% FFA, the water amount formed in the pretreatment reaction and that initially in the fat 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 synthetic mixture with 20% palmitic acid was about 1.3% water. So the initial water level of 0.2% does not seem to be great enough to explain the difference in the extent of reaction. The unknown, insoluble, and unsaponifiable material may also affect the pretreatment reaction. This material is almost certainly the cause of the interphase material that accumulates between the ester and wash water after transesterification with yellow grease. The interphase material will be discussed in a later section.

It was assumed in the synthetic mixture study that palmitic acid is one of the dominant fatty acids present in most vegetable oils and animal fats and reacts at the same rate as other fatty acids. However, animal fats also contain large amounts stearic acid (C18:0), oleic acid (C18:1), and linoleic acid (C18:2), as was seen in Table 5.19. The reaction rates of these fatty acids could be different than palmitic acid and this would explain the differences in the reaction rates between the two feedstocks. However, comparisons of the fatty acid distributions of feedstocks and finished esters are always very similar which indicates that the reactions do not seem to differentiate between specific fatty acids. 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.

5.3.2. Effect of Different Alkaline Catalysts on Transesterification

To investigate the continuation of the transesterification reaction of the yellow grease to completion, an additional quantity of pretreated yellow grease was prepared. The pretreatment consisted of a 1-hour reaction time, 5% sulfuric acid amount, and a 20:1 molar ratio for the first step, and a 40:1 molar ratio for the second step. Using these mixtures, the process was continued with different alkaline catalysts at room temperature for 8 hours. To investigate the effect of different catalysts, potassium hydroxide (KOH), sodium hydroxide (NaOH), sodium methoxide ($NaOCH_3$), and metallic sodium (Na) were used. The molar ratio was 6:1 and the catalyst amount was varied from 0.7 to 0.35% to hold constant the amount of pure metal in the catalyst. The molar ratio of alcohol and the catalyst amount were calculated for the transesterification based on the initial amount of fat in the yellow grease. Table 5.22

also shows the amount of pure metal used in the various catalysts. All samples met the total glycerin specification but the metallic sodium gave the best yield as seen in Table 5.22. The yield was calculated by dividing the final weight of ester by the initial weight of yellow grease.

Table 5.22: Effect of different catalysts on transesterification

Molar Ratios & Cat. Amount	*Catalyst Amount in Transesterification*	*Catalyst Amount as Metal Base*	*Total Glycerol (%)*	*Spe. Gravity*	*Yield (%)*
20:1; 40:1 (5% Cat.)	1% KOH	0.7% K	0.23	0.8729	74.8
20:1; 40:1 (5% Cat.)	0.5% KOH	0.35% K	0.23	0.8746	74.3
20:1; 40:1 (5% Cat.)	0.61% NaOH	0.35% Na	0.23	0.8741	81.2
20:1; 40:1 (5% Cat.)	0.82% $NaOCH_3$	0.35% Na	0.20	0.8735	80.5
20:1; 40:1 (5% Cat.)	0.35% Na	0.35% Na	0.20	0.8745	82.2

Our study was extended to investigate the necessity of separation of the alcohol-water mixture after the pretreatment process. The water amount created in the pretreatment will be diluted by using higher alcohol molar ratios and it would not effect the transesterification reaction. Therefore, we used a 30:1 molar ratio with 5% acid catalyst based on the FFA level for a 1-hour reaction. Then, the process was continued with alkaline catalyst (1% KOH+ neutralization amount) at a 6:1 molar ratio. As seen in Table 5.23, the acid value of the mixture before the transesterification reaction was 5.67 mg KOH/g. Although we used some extra alkaline catalyst to neutralize the acidity of the mixture, the total glycerin amount met the specification but the yield was 71.68%. The reasons for lower yield were probably the water in the mixture and more soap formation during the transesterification reaction.

Table 5.23: The methyl ester results prepared without separation in acid catalyst test

Molar Ratios & Catalyst Amount	*A.V. (mg KOH/g)*	*Catalyst Amount in Transesterification*	*Total Glycerol (%)*	*Sp. Gravity*	*Yield (%)*
30:1 (5% Cat.)	5.67	1% KOH	0.20	0.8736	71.68

5.3.3. Summary of the Preparation of Methyl Esters from Yellow Grease

The primary objective of this study was to prepare methyl esters from yellow grease. The 2-step acid-catalyzed reaction developed in the earlier part of the project was applied to the feedstock to reduce its acid value to less than 1 mg KOH/g. After the acid value was reduced to less than 1 mg KOH/g, the transesterification reaction was continued with several alkaline catalysts at room temperature for 8 hours. The completeness of the reaction was measured using the A.O.C.S Official method Ca 14-56 as before.

The following summary can be drawn from the study of biodiesel production from yellow grease with high FFA.

1. The two-step acid catalysis process was successful in decreasing the acid value of the yellow grease to less than 1 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.
2. A one-hour reaction time for each step of the 2-step acid catalyst process was found to be sufficient for yellow grease.
3. After decreasing the acid value of the mixture the alkaline catalyst transesterification gave good ester conversion. All biodiesel produced met the total glycerin specification regardless of the catalyst type or amount.
4. The alkaline catalyst type affects the ester yield and the best yield, 82.2%, was obtained with 0.35% metallic sodium.

5. The pretreatment reaction may occur in a 1-step acid catalysis process without separation and at a higher molar ratio. But for this case more excess alkaline catalyst is required to neutralize the acid level of the mixture in the transesterification reaction. This type of process also reduced the ester yield.

5.4. Preparation of Methyl Esters from Brown Grease

To investigate the usefulness of the process developed for yellow grease biodiesel production, the study was extended to preparation of methyl esters from actual brown grease with 33% FFA. The brown grease was obtained from the Simonsen rendering plant in Quimby, Iowa. As with the yellow grease, the first step in processing this material was to filter out the insoluble materials (such as meat and bone particles) at around 55°C or 60°C. Then, a three step acid-catalyzed reaction was applied to the feedstock to reduce its acid value to less than 2 mg KOH/g. The specific fat analyzed for this project had an acid value of 66.08 mg KOH/g which corresponds to a FFA level of about 33%. In the first two steps, the reaction conditions were a molar ratio of 20:1, 5% acid catalyst, and a 1-hour reaction time at 60°C. In the third step, the molar ratio of alcohol was increased to 40:1 as the catalyst percentage and the reaction time remained the same. The sulfuric acid and methanol amounts were based on the FFA level in the brown grease. After the acid value was reduced to less than 2 mg KOH/g, the transesterification reaction was continued with the alkaline catalyst at room temperature for 8 hours.

To compare a different alcohol type in the pretreatment of feedstock with high FFA, ethanol was also used at a 20:1 molar ratio and 5% catalyst for a 1-hour reaction at 75°C. It was found that the ethanol and water did not separate after the first step. Therefore the process could not be continued with ethanol. It was later determined that this was due to ethanol having a higher solubility in the ester.

The changes in the acid value of the mixtures are shown in Table 5.24 for three separate test runs. As seen in the table, the final values are very close to each other. After each step, the acid value of the brown grease mixture decreased to around 16 mg KOH/g, 5 mg KOH/g and 2 mg KOH, respectively.

Table 5.24: The acid values (mg KOH/g) of the feedstocks measured after each step with 5% catalyst amount and 1 hour reaction time at 60°C

Methanol Molar Ratio	*Run 1*	*Run 2*	*Run 3*
Before Test	66.08	66.08	66.08
1st Step (20:1)	16.17	15.72	16.40
2nd Step (20:1)	5.00	4.52	4.52
3rd Step (40:1)	1.97	1.92	1.97

5.4.1. Effect of Catalyst Amount on the Acid Value of Brown Grease

Three steps of pretreatment were considered to be undesirable. The extra step of pretreatment requires more time, more alcohol, and reduces the yield. To investigate whether the pretreatment could be accomplished in 2 steps, the work was extended to higher catalyst amounts in the pretreatment reaction. When the sulfuric acid catalyst amount was increased to 10%, the acid values after the first and second steps reduced to around 5 mg KOH/g and 2 mg KOH, respectively. The pretreatment consisted of a 1-hour 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 acid value of the mixture are shown in Table 5.25. By increasing the acid catalyst amount, very high levels of FFA can be processed with a 2-step pretreatment.

Table 5.25: 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

5.4.2. Effect of Different Alkaline Catalyst and Amounts on Transesterification

To investigate taking the transesterification reaction of the brown grease to completion, samples of pretreated brown grease were prepared using the 3-step pretreatment. Using this mixture, the process was continued with different alkaline catalyst amounts of sodium methoxide ($NaOCH_3$) at room temperature for 8 hours. As discussed in section 5.3.2, $NaOCH_3$ was found to be one of the strongest catalysts. $NaOCH_3$ also has the advantage that it can be purchased, in bulk, already premixed with methanol. This offers considerable safety and convenience over KOH which must be measured and dispensed manually. Therefore, $NaOCH_3$ was selected as the alkaline catalyst for the transesterification reaction. To investigate the effect of different catalyst amounts, the percentages of $NaOCH_3$ were 0.82%, 0.41%, 0.21%, 0.1% and 0.05%. The alkaline catalyst amounts were calculated as *% alkaline catalyst + a neutralization amount.* That is, the amount of catalyst added was the percentage given above plus an amount needed to neutralize the remaining FFA, assuming one mole of sodium methoxide to neutralize one mole of FFA. The alcohol molar ratio was 6:1. The molar ratio of alcohol and catalyst amount was calculated in the transesterification based on the initial amount of fat in the brown grease. Table 5.26 shows the total and free glycerin, specific gravity and yield of the methyl esters prepared. The yield was calculated by dividing the final weight of ester by the initial weight of brown grease.

In the first run, due to an excessively high catalyst amount, too much soap was formed and no separation happened, even after washing two times at the rate of 50% by volume of the mixture. As mentioned earlier, if too much catalyst is used in the transesterification reaction, it increases the soap formation. More soap emulsifies the mixture and causes difficulties in the ester separation and reduces the ester yield. As seen in the table, the best result in total glycerin, specific gravity, and yield was obtained with the 0.21% catalyst amount. When a lower catalyst than 0.21% was used, the reaction did not go to completion, and the ester did not meet the total glycerin specification. The specific gravity also started to increase. When the catalyst amount was increased to more than 0.21%, the total glycerin amount started to increase, and the yield was reduced due to soap formation.

Table 5.26: The effect of different catalyst ($NaOCH_3$) amounts on transesterification

Run No.	*Catalyst (%)*	*Total Glycerin (%)*	*Free Glycerin (%)*	*Specific Gravity*	*Yield (%)*
1	0.82	*	*	*	*
2	0.41	0.1595	0.0000	0.8757	51.91
3	0.21	0.1179	0.0000	0.8748	56.39
4	0.10	0.3257	0.0019	0.8787	55.36
5	0.05	0.4209	0.0016	0.8794	55.58

* No separation between glycerin and ester

Reactant mixtures produced with the 2-step pretreatment were also processed with different alkaline catalyst amounts at room temperature for 8 hours. To investigate the effect of different catalyst amounts, potassium hydroxide (KOH) with 0.5% and 0.25%, and sodium methoxide ($NaOCH_3$) with 0.41% and 0.21% were used. The actual alkaline catalyst amounts used were calculated as *% alkaline catalyst + the neutralization amount*. The alcohol molar ratio was 6:1. The results are shown in Table 5.27.

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 changed to $NaOCH_3$ at 0.21%, the total glycerin amount, the specific gravity of the ester and yield were 0.18%, 0.8748, and 75.1%, respectively. However, a further increase of the $NaOCH_3$ gave lower yield and higher total glycerin due to more soap formation. It was noted that the successful reaction with a 2-step pretreated sample gave a yield (75.1%) that was much higher than the highest yield found for the material pretreated with the 3-step process.

Table 5.27: The effect of different catalyst and amounts on transesterification after 2 steps pretreatment reaction

Run No.	*Catalyst (%)*	*Total Glycerin (%)*	*Free Glycerin (%)*	*Specific Gravity*	*Yield (%)*
6	0.5 (KOH)	1.91	-	0.8848	56.4
7	0.25 (KOH)	9.22	-	0.9014	-
8	0.41 ($NaOCH_3$)	0.19	0.004	0.8751	67.0
9	0.21 ($NaOCH_3$)	0.18	0.002	0.8748	75.1

5.4.3. Yield Analysis of the Methyl Esters Produced from Feedstock with High FFA

Due to the low yield after the pretreatment and transesterification reactions, the losses during the reactions were investigated. In this section, the sources for the losses in the reactions are discussed.

5.4.3.1. Effect of Pretreatment Step Number and Alkaline Catalyst on the Methyl Ester Yield

As summarized in Table 5.28, the yield was increased when the brown grease was pretreated in two steps instead of three. The losses in the final step of either the 3-step or the

2-step processes may not be lost if the alcohol mixture is not 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. 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-water mixture, the remaining material was weighed. The fat and ester amounts removed in the pretreatment steps are shown in Table 5.28. Apparently, 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. When the number of steps was reduced from three to two, the yield was increased. Therefore, it was determined that a study of the solubility of the fats in methanol would be a valuable extension of this study. This subject will be discussed in the next section.

The catalyst amount used in transesterification was another factor that affected the low yield. When a very high amount of 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 is not currently known but it is insoluble in both 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. 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 material decreased when the number of pretreatment steps was decreased from three to two.

The catalyst type also had an effect on the transesterification of the feedstock. To investigate the different catalyst effects potassium hydroxide (KOH) and sodium methoxide ($NaOCH_3$) were used. The $NaOCH_3$ provided a complete reaction with 0.41% and 0.21%, catalyst amounts. At the same conditions the KOH did not give acceptable results with 0.5 and 0.25% catalyst amounts. These results confirmed that $NaOCH_3$ is much more effective than KOH. The amount of interphase material decreased when the $NaOCH_3$ catalyst percentage was decreased from 0.41% to 0.21%, in the 2-step pretreatment.

Table 5.28: The losses in pretreatment and transesterification

Run No.	***Catalyst %***	***Feedstock (g)***	***Ester (g)***	***Yield (%)***	***Interphase (g)***	***The Loss in Pretreatment***		
						1st Step (g)	***2nd Step (g)***	***3rd Step (g)***
1	0.82 $NaOCH_3$	400	-	-	326.18	38.26	20.63	9.85
2	0.41 $NaOCH_3$	300	151.83	51.91	91.24	26.07	16.87	8.67
3	0.21 $NaOCH_3$	300	164.95	56.39	84.21	26.07	16.87	8.67
4	0.10 $NaOCH_3$	300	161.94	55.36	85.96	24.96	18.09	5.75
5	0.05 $NaOCH_3$	300	162.58	55.58	93.20	24.96	18.09	5.75
6	0.5 KOH	300	163.57	56.40	100.83	31.94	4.74	-
7	0.25 KOH	300	47.21	-	218.80	31.94	4.74	-
8	0.41 $NaOCH_3$	300	200.90	66.97	60.40	31.11	5.23	-
9	0.21 $NaOCH_3$	300	225.36	75.12	37.12	31.11	5.23	-

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

To understand the losses in the pretreatment process, the solubility of the reactants in methanol was studied as a function of temperature. Soybean oil, lard, yellow grease methyl ester (YGME), yellow grease, and brown grease were mixed separately with equal amounts of methanol by volume at 60°C for 1 hour. No catalyst was added so no reaction was assumed to occur. 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 equal samples were drawn from the bottom and top of the mixture. Then the samples were heated on a hot plate to evaporate the methanol. After evaporation, the percentage of methanol in the lower phase and the upper phase were calculated. Figure 5.18 represents 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 different oils with different FFA levels (9% and 33%) are compared, it can be noted that the solubility of the oil increases for the oil with higher FFA. The solubility of the yellow grease methyl ester in methanol was the highest among the samples. These data show why the yield decreased when the higher FFA feedstocks were processed. At the higher FFA levels, the methanol-water mixture removed during pretreatment was carrying a greater

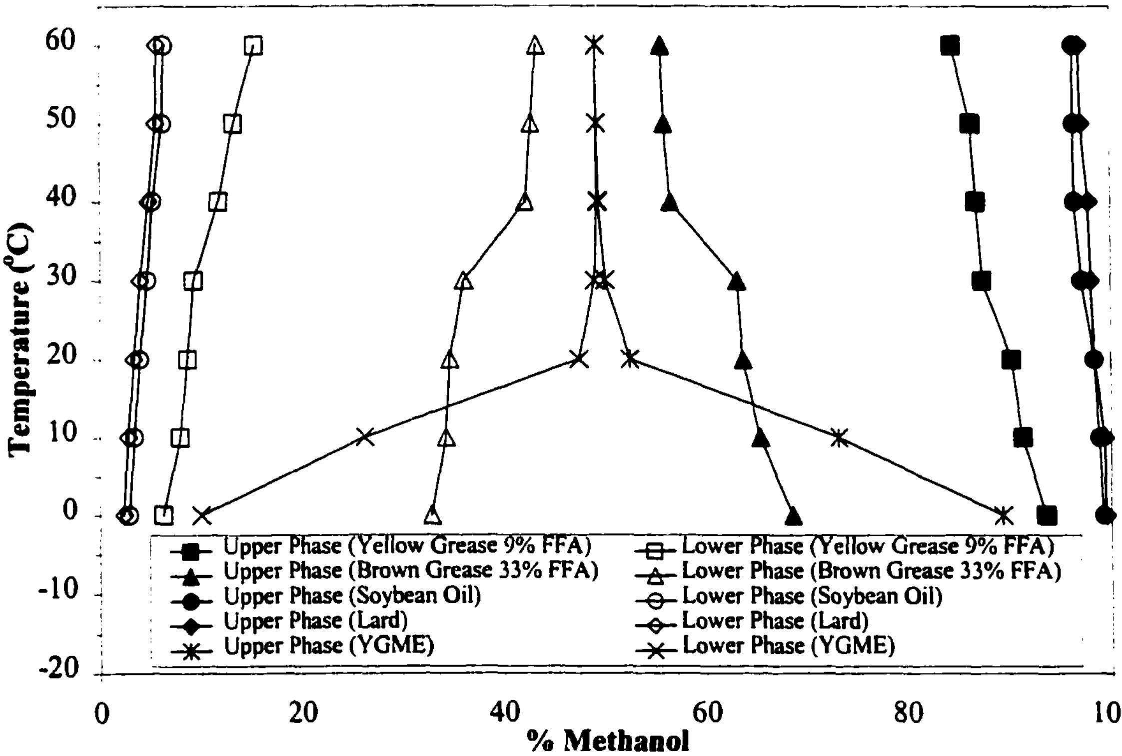


Figure 5.18: Solubility of soybean oil, lard, YGME, yellow grease and brown grease in methanol

amount of fat as well as a significant portion of the methyl ester (YGME) that may have been produced. This problem can be addressed by evaporating the methanol and water from the material removed during pretreatment and returning the residue to the process stream.

5.4.4. Summary of the Preparation of Methyl Esters from Brown Grease

The objective of this part of the study was to demonstrate that methyl esters could be produced from brown grease with high FFA. Two different approaches involving three steps of pretreatment (with 5% catalyst) and 2 steps of pretreatment (with 10% catalyst) were applied to the 33% FFA brown grease to reduce its acid value to less than 2 mg KOH/g. After the acid value was reduced to less than 2 mg KOH/g, the transesterification reaction was continued with sodium methoxide ($NaOCH_3$) as the alkaline catalyst at room temperature for 8 hours. The following summary can be drawn for biodiesel production from brown grease with 33% FFA.

1. The three-step pretreatment process with 5% catalyst amount was successful in decreasing the acid value of the brown grease to less than 2 mg KOH/g.
2. When 10% sulfuric acid was used in the pretreatment reaction, the number of steps was reduced from three to two.
3. After decreasing the acid value of the brown grease, the alkaline catalyst transesterification gave good ester conversion and the biodiesels met the total and free glycerin specification.
4. The yield percentage was increased when the number of pretreatment steps was reduced from three to two.
5. It was observed that the alkaline catalyst amount and type affects the transesterification

reaction and yield. $NaOCH_3$ is much stronger than KOH. The best result was obtained with 0.21% $NaOCH_3$ in the 2-step pretreatment and yield, total glycerin, and specific gravity were 75.12%, 0.1772%, and 0.8748, respectively.

6. Increasing the number of steps of pretreatment reduces the ester yield due to the solubility of the fat and ester in methanol. Recovery of this lost material will be essential for maximum process yield.

5.5. Soap and Catalyst Analysis in Washing Process of the Methyl Esters

If FFAs are present in the feedstock when an alkaline catalyst is used for transesterification, they will react with the catalyst to form soap. These soaps are then removed in the washing process. The washing process also removes any residual catalyst in the ester. To investigate the effectiveness of the washing process, samples from the ester phase, the wash water, and the glycerin were collected and the soap and catalyst amounts were measured. The test method is described in Appendix C.

Three different methyl esters were produced from saturated vegetable oil, lard, and pretreated yellow grease with 9% FFA level. The percentage and amounts of soap and catalyst in the ester, wash water, and glycerin are shown in Table 5.29. When the esters were washed, after 3 washing cycles, there was no difference in the soap amount in further washing waters. However, a larger soap amount was found in the wash waters of the lard and yellow grease esters. When the total soap formation in the reaction was compared, the yellow grease methyl ester reaction produced the highest soap amount as seen in the table. Table 5.29 also shows that most of the soap and catalyst are removed with the glycerin phase. To check the accuracy of the measurements, a mass balance was performed on the sodium as shown in Table 5.30. The total amount of sodium (Na) measured in the output was very close to the amount of sodium input as catalyst. This confirms that 95.1 – 97.0% of the sodium added with the catalyst is removed with the glycerin, 1.6 - 2.5% is removed from the ester in the wash water, and 0.27 – 0.33 % remains in the ester after washing.

Table 5.29: Analysis of the catalyst amount and soap produced in the reaction

Sample	***Saturated Vegetable Oil***		***Lard***		***Yellow Grease***	
	% Cat.	% Soap	% Cat.	% Soap	% Cat.	% Soap
Ester	0	0.015	0	0.013	0	0.014
Wash Water	-	-	-	-	-	-
1	0	0.061	0	0.053	0	0.091
2	0	0.022	0	0.039	0	0.041
3	0	0.016	0	0.037	0	0.026
4	0	0.015	0	0.036	0	0.020
5	0	0.015	0	0.034	0	0.020
6	0	0.015	0	0.034	0	0.020
Glycerin	4.327	2.172	3.962	3.547	2.203	6.904

Table 5.30: Mass balance of the catalyst used in the transesterification reaction

	Saturated Vegetable Oil		***Lard***		***Yellow Grease***	
	Catalyst		***Catalyst***		***Catalyst***	
	Amount	***%***	***Amount***	***%***	***Amount***	***%***
Total Input of $NaOCH_3$	3.280 g	-	3.280 g	-	3.280 g	-
Total Input of Na	1.396 g	100	1.396 g	100	1.396 g	100
Methyl Ester	0.0046 g	0.33	0.0039 g	0.28	0.0037 g	0.27
Glycerin	1.3540 g	97.0	1.3269 g	95.1	1.3423 g	96.2
Wash Water	0.0217 g	1.55	0.0348 g	2.49	0.0327 g	2.34
Total output of Na	1.3803 g	98.88	1.3656 g	97.87	1.3787 g	98.81

5.6. Test System Setup for Pilot Plant Scale Biodiesel Production

After finding the best strategy for the small-scale transesterification of feedstocks with high FFA, a pilot plant was designed to implement the strategy. The pilot plant has been assembled at the Iowa Energy Center's Biomass Energy Conversion Center (BECON) in Nevada, Iowa. The front and back views of the pilot plant are shown in Figures 5.19 and Figure 5.20, respectively. This pilot plant has 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 and equipment of the pilot plant are described below.

Half-inch stainless steel tubing was used to connect all components for the entire pilot plant. To get flexibility in some places, ½ inch teflon-lined tygon tubing was used. For both units, an air-operated pump was used to pump methanol. Methanol was supplied directly from 55-gallon drums and one ½ hp pump was used to drain waste water and alcohol mixture from the tank.

5.6.1. Pretreatment Unit in the Pilot Plant

A schematic of the pretreatment unit is shown in Figure 5.21. Warm feedstock with high FFAs (yellow grease or brown grease) can be delivered to the BECON facility by truck. Separate 500-gallon, cone bottom, insulated storage tanks are available for the vegetable oil and animal fat feedstocks. Since the animal fat feedstock solidifies at room temperature, it needs to be heated before pretreatment. The tank of animal fat feedstock can be kept

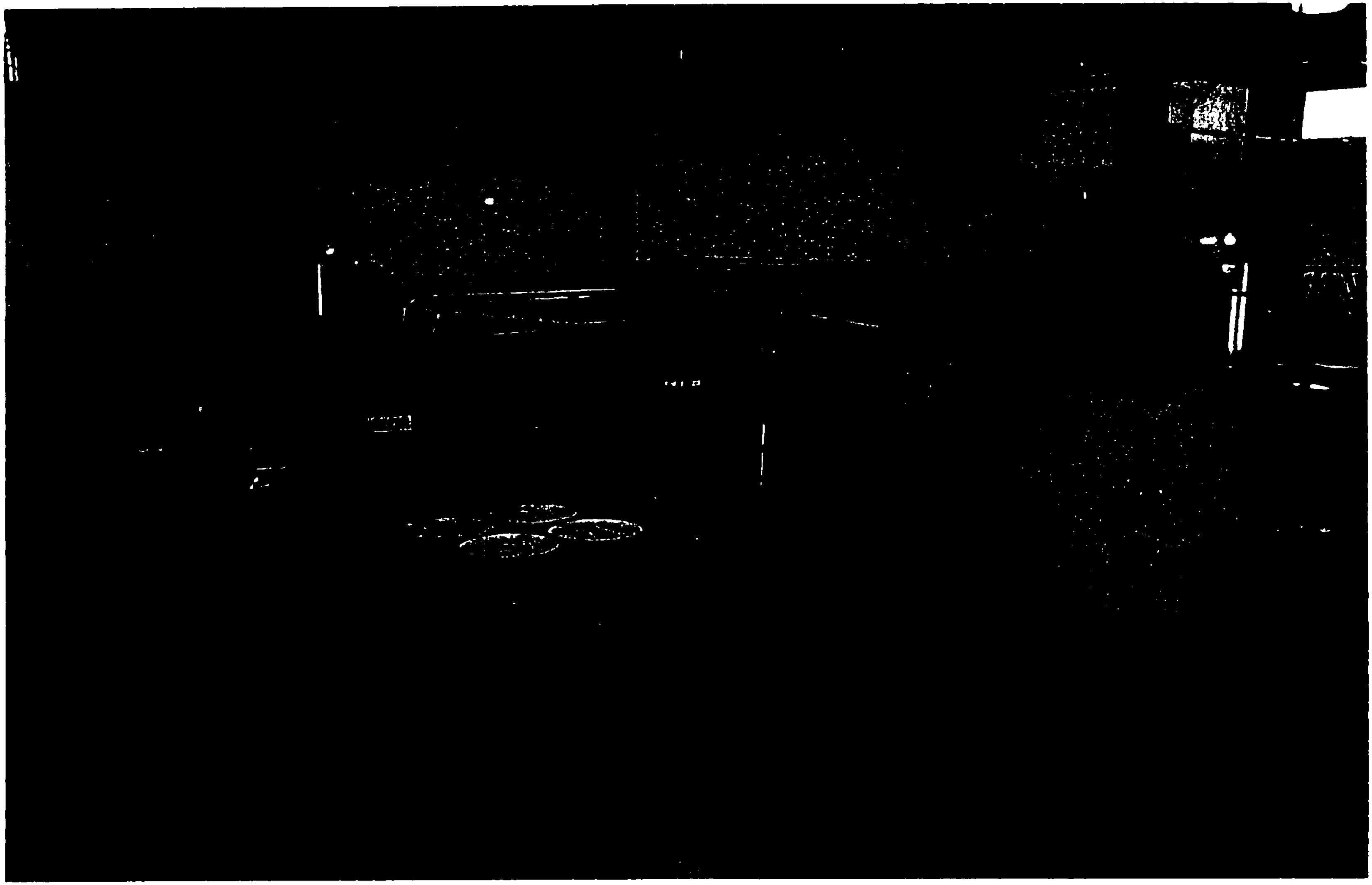


Figure 5.19: The front view of the pilot plant

Figure 5.20: The back view of the pilot plant

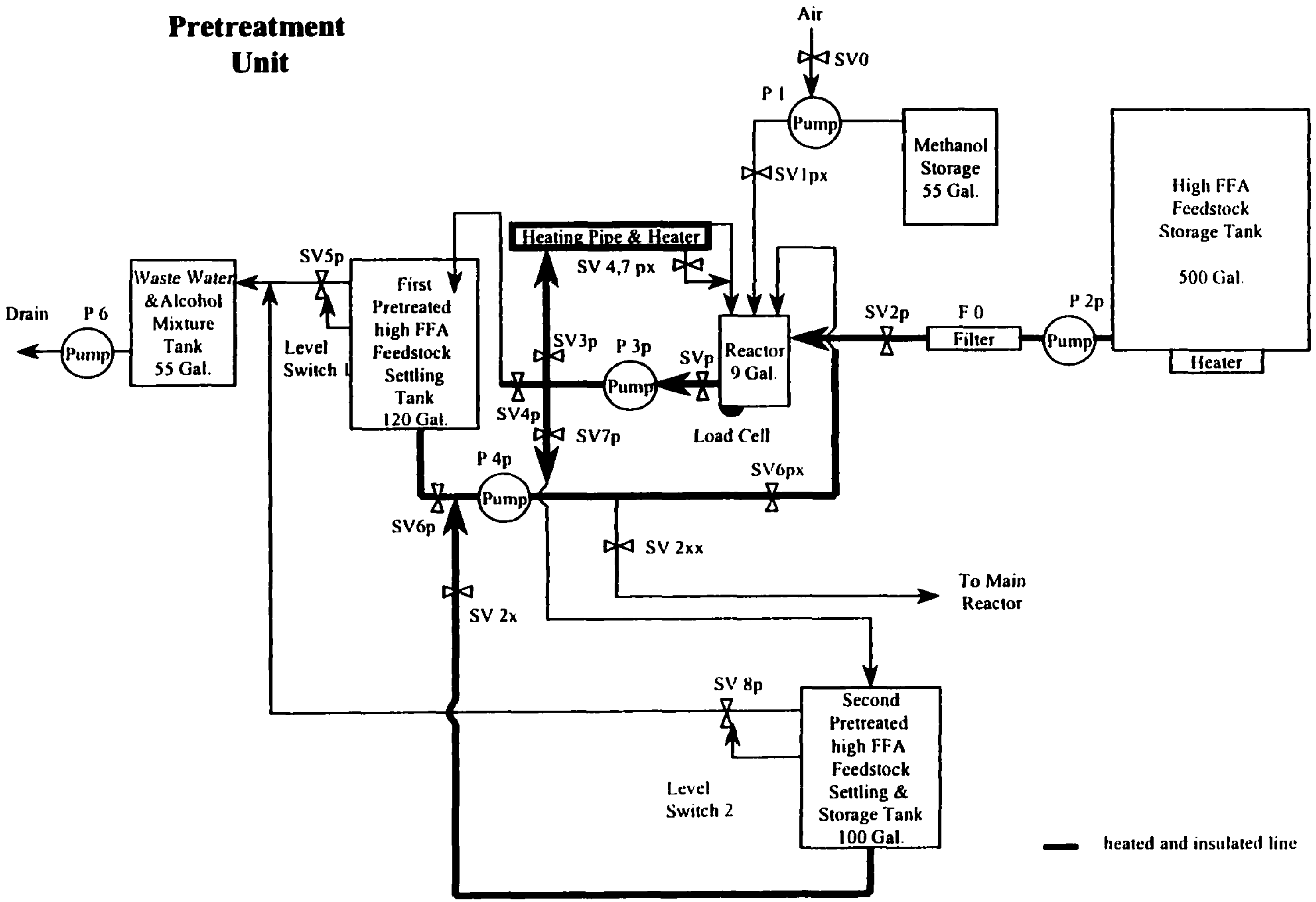


Figure 5.21: Flow diagram of the pretreatment unit of the pilot plant

at 55-60°C using a 1200 watt/480 volts heater, a 1/3 hp recirculating pump, and a thermostat. A 20-micron cellulose filter is used to remove insoluble materials, such as meat and bone particles, from the yellow or brown grease. The pump, identified on the schematic as P 2p transfers the feedstock to the 9-gallon stainless steel pretreatment reaction tank. A thermocouple mounted in the reaction tank checks the reaction temperature during the pretreatment process. A load cell weighs the amount 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). A ½ hp pump (P 3p) is used for recirculating and transferring the mixture to the settling tanks. The temperature of the mixture during pretreatment needs to be around 60°C. For this purpose, an insulated, 3 inch diameter by 5 feet long, stainless steel heating pipe with a 3000 watt/480 volts heater is used.

When the FFA reacts with alcohol to form ester, water is formed in the products. Therefore, it is necessary to separate the water from the pretreated material since it will inhibit further reaction. A 120-gallon stainless steel settling tank is used to separate the alcohol-water mixture from the feedstock after pretreatment. Level switches mounted in the tanks control solenoid valves to drain the alcohol-water mixture to a 50-gallon waste water tank. For the second step of pretreatment, another 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. Again, pump P 3p recirculates the mixture for 1 hour at 60°C and then pumps it to the second settling tank which is a 100-gallon stainless steel tank. After reducing the acid level of the feedstock to less than 1%, it is transferred from the second pretreatment settling tank to the main reaction tank for transesterification using pump P 4p.

5.6.2. Transesterification (Main) Unit in the Pilot Plant

A schematic of the main reaction unit is shown in Figure 5.22. After soybean oil is purchased and delivered to the BECON facility, it is stored in the 500-gallon, cone bottom tank at room temperature. If soybean oil is used for transesterification reaction, the tank's 1/3 hp 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. The main transesterification reaction takes place in a 70-gallon, stainless steel reaction tank with a ½ hp explosion-proof mixer, which has a fixed speed of 1750 rpm. A load cell, which was mounted on one leg of each reaction tank, measures the reactant amounts. Methanol is added to the reaction tank using the air-operated pump P 1. After preparing the alcohol solution with the catalyst, it is added to the reaction tank. Then, the reactants mix for 8 hours, and the mixture is transferred to a 130-gallon cone bottom tank for glycerin separation and ester washing. A load cell mounted on the bottom of one leg of the tank measures the glycerin amount, the washing water amount, and the amount of ester produced. A Micro Motion brand density meter installed at the exit of the separation tank quantifies the glycerin, water, and ester in the separation processes. A pump (P 4) transfers the glycerin to the glycerin storage container, a 55-gallon stainless steel tank and then the ester is washed to remove residual catalyst and soap in the ester.

The hardness of the city water of Nevada, Iowa has been measured to be 27.4 grains per gallon by MVTL Laboratories, Inc., Nevada, Iowa. For better washing, a water softener and a 50-gallon, 4500 watt/110 volts 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.

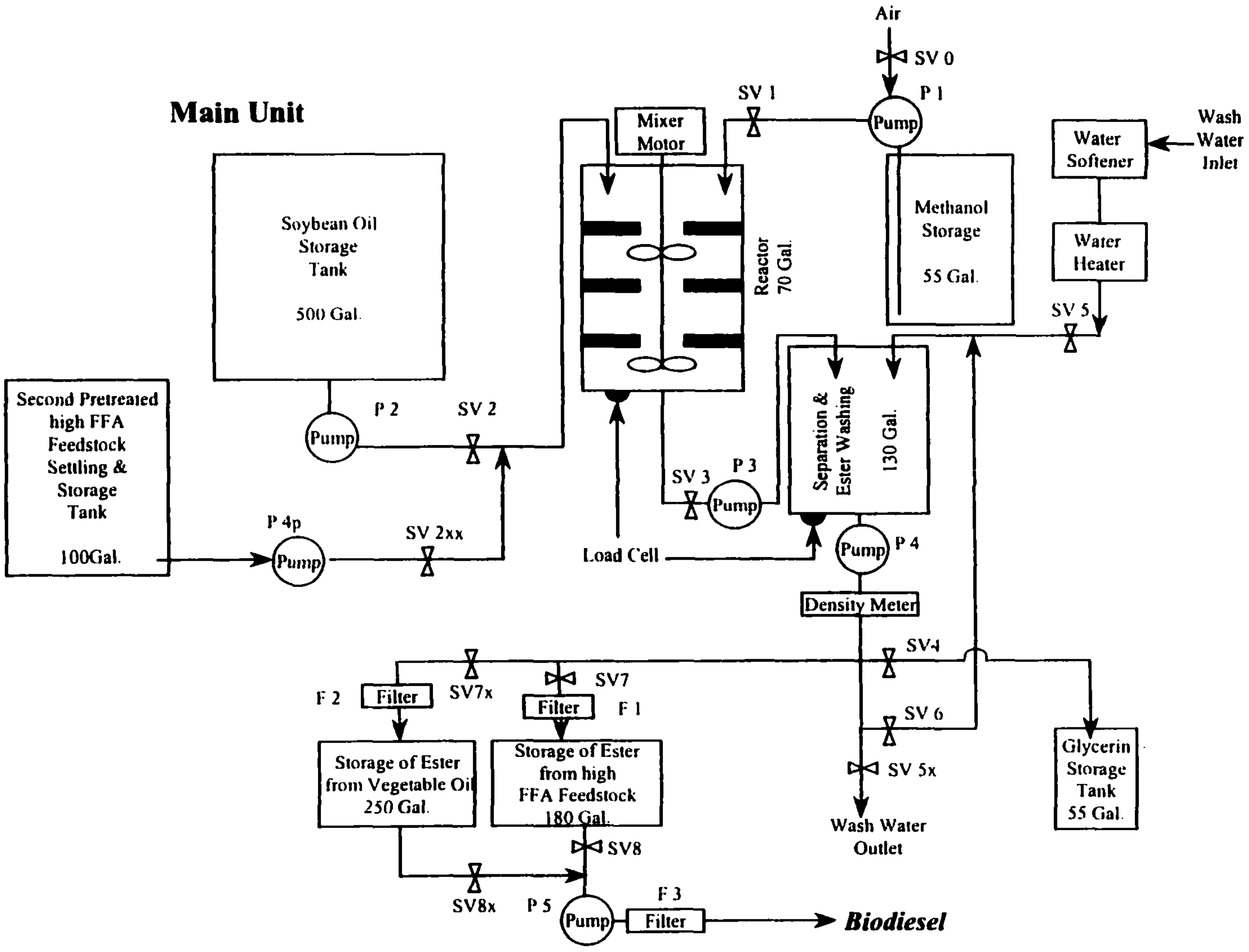


Figure 5.22: Flow diagram of the transesterification (main) unit of the pilot plant

The same pump (P 4) is used to recirculate the washing water as to transfer it to the waste outlet, and move the finished ester to the storage tanks. Two separate storage tanks, a 250-gallon stainless steel tank and a 180-gallon stainless steel tank, are used for the biodiesel from high FFA feedstock and the biodiesel from vegetable oil, respectively. Another pump (P 5) is used to transfer the biodiesel to external storage tanks. The esters are filtered with 20-micron cellulose filters when pumped to the external storage tanks.

5.7. Pilot Plant Operation and Analysis

The pilot plant described in the previous section was used for preparation of large amounts of methyl esters from soybean oil and rendered grease. The pilot plant process was validated using soybean oil, yellow grease, and finally brown grease. The following sections describe the adaptation of the small-scale processes to the large-scale biodiesel production in the pilot plant. This adaptation process will be presented through the use of 3 specific case studies of the use of the pilot plant to produce biodiesel from different feedstocks.

5.7.1. Large Scale Biodiesel Production from Soybean Oil (Case Study 1)

The first case study will describe using the pilot plant to produce biodiesel from soybean oil. To prepare biodiesel from soybean oil in the pilot plant, the following procedure was used. One percent KOH was dissolved in methanol at room temperature in the main reaction tank. The catalyst amount was based on the weight of vegetable oil and the molar ratio of alcohol to oil was 6:1. Then, the vegetable oil was added to the reaction tank at room temperature. The transesterification process was continued at room temperature for 8 hours. The reaction completion was monitored and the data for soybean oil are shown in Table 5.31 and Figure 5.23. As seen in Table 5.31, the reaction completion did not change very much

Table 5.31: Total glycerin and specific gravity change during the transesterification of soybean oil

Time (hours)	*Total Glycerin (%)*	*Specific Gravity*
0	11.07	0.9212
1	1.09	0.8849
2	0.79	0.8843
3	0.69	0.8834
4	0.62	0.8832
5	0.56	0.8825
6	0.54	0.8825
7	0.53	0.8826
8	0.52	0.8826

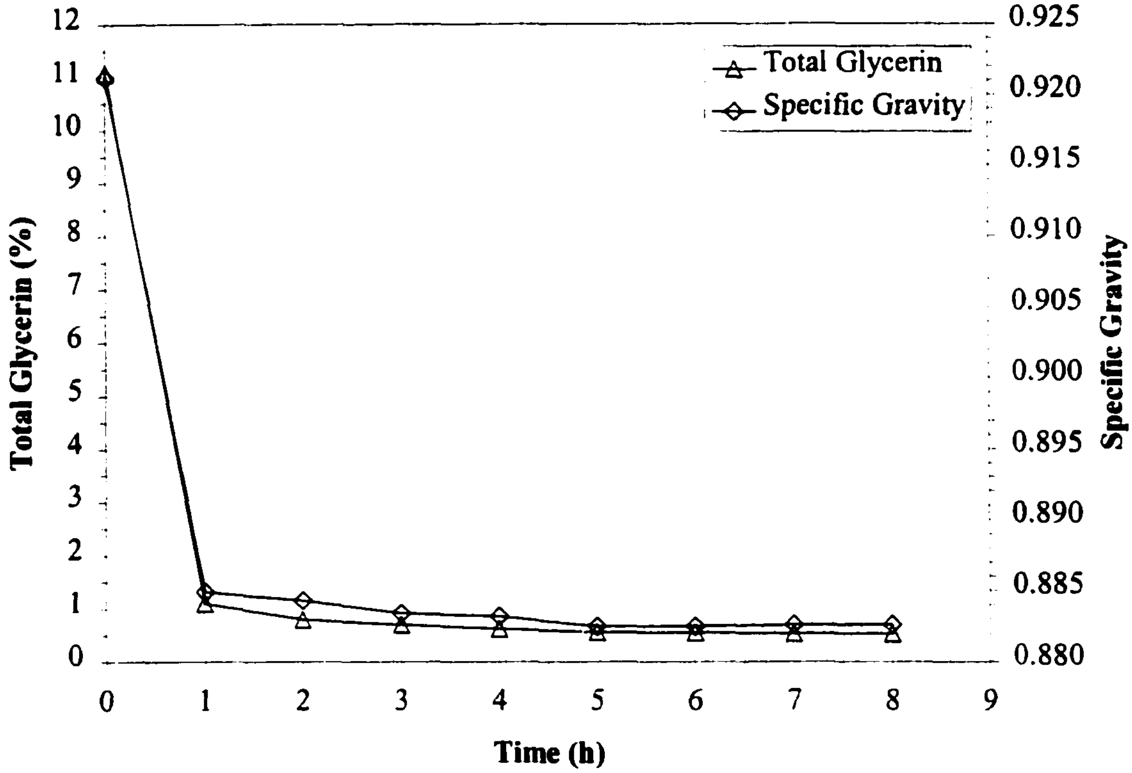


Figure 5.23: Total glycerin and specific gravity change during the transesterification of soybean oil

after 4 hours. 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%.

The ingredient amounts for transesterification of one batch are shown below.

For One Batch:

181.18 kg soybean oil

39.40 kg methanol (6:1 molar ratio)

1.81 kg KOH (1%)

After 8 hours, the mixture was pumped to a separation tank, and the ester and glycerin layers were allowed to separate in the tank overnight. The glycerin that collected at the bottom of the tank was pumped to the glycerin tank and the methyl esters were washed four times with softened warm water (40°C) to remove the excess alcohol and catalyst. Each washing required 30 minutes and the amount of water was 50% by volume of the ester. After extracting the wash water, the ester was pumped to the storage tank. The completeness of the reaction was measured using the method described earlier but the samples did not meet the total and free glycerin specifications. Therefore, the biodiesel was reacted again with an alcohol solution with 0.1% KOH, and washed four times again. This time the alcohol amount used was at a 3:1 molar ratio based on the initial amount of oil. The specific gravity of the ester at room temperature was measured after each batch and is also shown in Table 5.32. After the second step of transesterification, the total glycerin level of the biodiesel was very low and easily met the 0.24% specification.

The soybean oil used in the transesterification described above was partially refined soybean oil containing some residual phosphorus, except for the oil used in the third run. To investigate whether a refined oil would behave differently in the transesterification reaction, 30 gallons of soybean oil was purchased from the local food store. As shown in the table, the third run has a higher yield than those of others. The reason was probably that in the third run the soybean oil was refined and bleached, while the first two runs used partially refined soybean oil containing phosphorus. Freedman et al. [44] has stated that the phosphorus in the oil leads to catalyst destruction and reduces the ester yield. However, the total glycerin level with the refined and bleached oil was still too high to meet the specification without an extra transesterification reaction.

In run 4, a different method was used for the two-part transesterification reaction. One fourth of the methanol solution was held back to use later. Then, the vegetable oil at room temperature was added. The reactants were mixed for 4 hours at atmospheric pressure and room temperature. After 4 hours, the mixture was settled for 30 minutes and the glycerin that collected at the bottom of the reactor was pumped to the separation tank. Then the methanol solution that had been held back was added, and the reaction was continued for another 3 hours. This procedure gave very low levels of total glycerin as shown in Table 5.32. 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. However, it did not explain why the pilot plant was not able to provide low total glycerin levels with a single reaction.

5.7.2. Large Scale Biodiesel Production from Yellow Grease (Case Study 2)

This section describes a case study on the use of the pilot plant to produce biodiesel from yellow grease. The first step in the processing of yellow grease was to filter out the insoluble materials, such as meat and bone particles, at around 55-60°C. Then, the two step

Table 5.32: Measured values of the biodiesel prepared from soybean oil

Run No.	*Reaction*	*Total Glycerol (%)*	*Free Glycerin (%)*	*Spe. Gravity*	*Yield (%)*
1	After 1st	0.50	-	-	-
	After 2nd	0.02	0.0144	0.8816	94.6
2	After 1st	0.48	-	-	-
	After 2nd	0.03	0.0207	0.8805	94.7
3	After 1st	0.52	-	-	-
	After 2nd	0.06	0.0207	0.8818	97.2
4	2 Step	0.07	0.0021	0.8811	94.8

acid-catalyzed reaction, developed in the earlier part of the project, 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 a FFA level of about 9%. For the yellow grease used, the saturated palmitic and stearic acid amounts were 23.24, and 12.96%, respectively.

The pretreatment unit in the pilot plant has a 20-kg feedstock capacity for each batch. The ingredient amounts at each stage for one batch are shown in Table 5.33.

After pumping the required amount of filtered yellow grease at 60°C into the pretreatment reaction tank, the methanol solution with sulfuric acid was manually added to the reaction tank. The first pretreatment consisted of 5% sulfuric acid and a 20:1 molar ratio of methanol, based on the measured FFA amount. The mixture was recirculated for one hour through the heating pipe, which kept the mixture temperature between 55°C and 60°C. After 1-hour of reaction the mixture was transferred to the first stage settling tank to separate the

Table 5.33: Ingredient amounts used in the pretreatment reaction of the yellow grease with 9% FFA for one batch

Reactant	*1st Stage*	*2nd Stage*
Feedstock	20 kg	20 kg
Methanol	4.35 kg	2.13 kg
Sulfuric Acid	0.087 kg	0.021 kg

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 feedstock in 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 one hour through the heating pipe to keep the temperature between 55°C and 60°C. After one hour of reaction 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 was so low (less than 0.1%) that it would not 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% $NaOCH_3$ + neutralization amount) at a 6:1 molar ratio of methanol. 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. 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 hours.

The ingredient amounts for transesterification of the pretreated yellow grease for one batch are shown in Table 5.34. The first column of numbers was based on the assumption that the water-alcohol mixture would be removed after the second step of pretreatment. The second column reflects the amounts with the water-alcohol mixture retained which was the actual process used.

Table 5.34: Ingredient amounts for transesterification of pretreated yellow grease for one batch

	Amount (kg) (If alcohol-water mixture is)	
Reactant	***removed***	***retained***
Pretreated Yellow Grease	164	176
Methanol	32.64	32.64
$NaOCH_3$ (0.82%)	1.22	1.22
$NaOCH_3$ (to neutralize)	0.23	0.28

Samples of the reacting mixture were removed at one hour intervals and analyzed for total glycerin to track the progress of the reaction. The results are shown in Table 5.35 and Figure 5.24. Most of the reaction occurs in the first hour and the reaction appears to have reached equilibrium after 4 hours.

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, the separation did not occur. Therefore, the mixture was washed four times for 30 minutes with soft warm water to remove the glycerin, excess alcohol, and catalyst. For each washing, the amount of water was 50% by volume of the ester. After the 4th washing step, the interphase material which accumulates 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.

As could be seen in Table 5.35, the samples did not meet the total and free glycerin specifications. Therefore, the biodiesel was reacted one more time with an alcohol solution with 0.1% catalyst, and washed four times again. This time the alcohol amount used was at a 3:1 molar ratio based on the initial amount of fat in the yellow grease. After this process, the biodiesel met the total glycerin specification. The measured values for three separate runs after the 2nd reaction step are shown in Table 5.36.

Table 5.35: Total glycerin and specific gravity change during the transesterification of yellow grease after pretreatment

Time (hours)	*Total Glycerin (%)*	*Specific Gravity*
0	10.36	0.9032
1	1.73	0.8792
2	1.15	0.8785
3	0.90	0.8778
4	0.75	0.8764
6	0.76	0.8764
8	0.67	0.8763

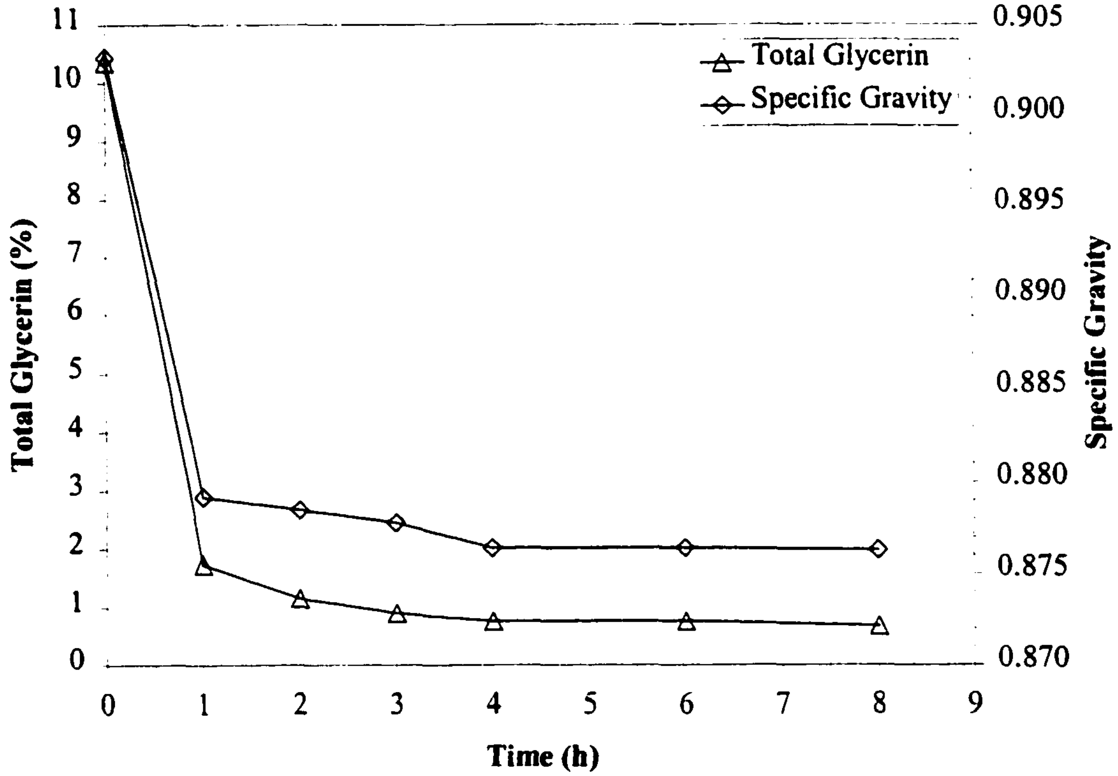


Figure 5.24: Total glycerin and specific gravity change during the transesterification of yellow grease after pretreatment

Table 5.36: Measured values of the biodiesel prepared from yellow grease

Run No.	*Reaction*	*Total Glycerin (%)*	*Free Glycerin (%)*	*Spe. Gravity*	*Yield (%)*
1	After 1st	0.66	-	0.8756	-
	After 2nd	0.22	0.0310	0.8752	82.8
2	After 1st	0.67	-	0.8763	-
	After 2nd	0.23	0.0392	0.8749	82.3
3	After 1st	0.62	-	0.8760	-
	After 2nd	0.23	0.0145	0.8748	82.2

In an attempt to understand the reason for the initially poor conversion in the reaction, saturated vegetable oil, lard, and pretreated yellow grease were transesterified under laboratory conditions. The saturated vegetable oil (Crisco) and lard were purchased from a local store. These tests were conducted to determine whether the higher saturation level of the yellow grease was the cause of the incomplete reaction. The saturated vegetable oil and lard were expected to be as saturated as the yellow grease if not more saturated. The results are shown in Table 5.37. Although the total glycerin levels are somewhat high for these feedstocks, all three esters met the total glycerin requirement. Apparently, the saturation level of the feedstock was not the cause of the high total glycerin levels noted after one reaction in the pilot plant. Moreover, since the total glycerin level of the yellow grease was acceptable in the small-scale laboratory tests, the poor conversion of the yellow grease in the pilot plant was attributed to a problem of scaling the laboratory process up to the pilot plant size.

Table 5.37: Transesterification results of different saturated feedstocks

Type of Feedstock	*Total Glycerin (%)*	*Free Glycerin (%)*	*Specific Gravity*	*Yield (%)*
Yellow Grease	0.24	0.0435	0.8712	92.5
Lard	0.24	0.0517	0.8678	99.4
Crisco	0.21	0.0000	0.8750	100.0

5.7.3. Effect of Mixing

One of the main variables effecting the transesterification reaction is the mixing rate. In the pilot plant, a high-speed mixer has been used. However, it was observed that in some cases, the entire body of the mixture was turning in the reaction tank as a single mass. Therefore, the reactants could not mix effectively. This was not a problem in the transesterification of feedstocks on the laboratory scale, but poor mixing was apparently a problem in the pilot plant-scale transesterification. For better mixing, stationary vanes were welded to the inside of the reaction tank which stopped the turning of whole body of mixture during the reaction. After the addition of the stationary vanes, one more transesterification batch of pretreated yellow grease was prepared. It was observed that the mixing was better than the previous runs. The test results are shown in Table 5.38. The total glycerin and yield were now almost equivalent to the laboratory scale testing and met the total glycerin specification of 0.24%.

Table 5.38: The effect of mixing on the transesterification of pretreated yellow grease

Run No.	*Total Glycerin (%)*	*Free Glycerin (%)*	*Specific Gravity*	*Yield (%)*
Before the vanes	0.62	-	0.8760	82.0
After the vanes	0.23	0.0186	0.8760	90.2

5.7.4. Effect of Washing Number

After the glycerin separation, the methyl esters must be washed with water to remove the excess alcohol, catalyst, and glycerin. Previous studies of the production of methyl ester from soybean oil [14] have shown that after being washed four times, the percentage of soap and catalyst in the wash water has stopped changing. However, for methyl ester produced from yellow grease, the test results indicated that washing four times might not be enough to meet the glycerin specification. Therefore, the methyl ester produced from yellow grease was washed six times at the rate of 50% by volume of the ester. The reason for more washing might be due to the lack of separation of the glycerin from the ester after the overnight settling. This means that the washing process must remove all of the glycerin from reactants instead of only a small fraction. The effect of washing number is shown in Table 5.39.

Table 5.39: The effect of washing number on glycerin amount and specific gravity of methyl ester produced from pretreated yellow grease

Washing Number	*Total Glycerin (%)*	*Free Glycerin (%)*	*Specific Gravity*
4 Times	0.29	0.124	0.8780
6 Times	0.23	0.019	0.8760

5.7.5. Large Scale Methyl Ester Production from Brown Grease (Case Study 3)

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. The two step acid-catalyzed reaction developed in the earlier part of this study (10% sulfuric acid case) was applied to the feedstock to reduce its FFA level to less than 1%. As was discussed in section 5.4.2, $NaOCH_3$ was found to be capable of tolerating almost 1% FFA level in the transesterification reaction. The brown grease analyzed for this study had an acid value of 79.20 mg KOH/g which corresponds to a FFA level of almost 39.2%. The fatty acid distribution of the brown grease is shown in Table 5.40. The saturated palmitic and stearic acid amounts were 22.83 and 12.54%, respectively. For comparison, the FFA distributions of the yellow grease with 9% FFA and soybean oil considered in the first two case studies are also given in Table 5.40.

As seen in Table 5.40, the saturated fatty acid percentages in the ester after transesterification were almost the same as the respective feedstock. This means that saturation level did not effect the transesterification reaction and all fatty acids react with essentially the same rate.

For the pretreatment reaction of the brown grease with 39.6% FFA in the pilot plant, the ingredient amounts at each stage for one batch are shown in Table 5.41.

Table 5.40: Fatty acid composition of the brown grease, yellow grease, and soybean oil and their methyl esters produced in pilot plant

Product	***Carbon Chain (%)****										***Unknown Components***	***Sat. (%)***
	C14:0	C15:0	C16:0	C16:1	C17:0	C18:0	C18:1	C18:2	C18:3	C20:0		
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

*Measured by Woodson-Tenent Laboratories, Inc., Des Moines, IA.

Table 5.41: Ingredient amounts used in the pretreatment reaction of the brown grease with 39.6% FFA for one batch

Reactant	***1st Stage***	***2nd Stage***
Feedstock	15 kg	25 kg
Methanol	14.85 kg	4.34 kg
Sulfuric Acid	0.590 kg	0.087 kg

After pumping the required amount of brown grease at 60°C into the pretreatment reaction tank, the methanol solution with sulfuric acid was added manually to the reaction tank. The first pretreatment consisted of 10% sulfuric acid, and a 20:1 molar ratio of methanol based on the 39.6% FFA measurement. The mixture was recirculated for one hour through the heating pipe which kept the mixture temperature 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 affect the next reactions. At the end of the first stage, the average acid value of the feedstock was measured to be 6.96 mg KOH/g.

In the second stage of the pretreatment, the feedstock in the first stage-settling tank was taken back to the pretreatment reaction tank and the additional methanol and sulfuric acid solution were added in the amounts shown in Table 5.41. 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 one hour through the heating pipe where the temperature was kept between 55°C and 60°C. After the reaction, the mixture was taken to the second stage settling tank. The water formation (less than 0.1%) in this stage was so low that it would not affect the transesterification reactions. Therefore, the alcohol-water mixture was not removed before the main reaction. At the end of the second stage, the average acid value of the feedstock was measured to be 1.54 mg KOH/g. The acid value changes in the pretreatment reaction are shown in Table 5.42.

The ingredient amounts for the main transesterification of the pretreated brown grease are shown in Table 5.43 for one batch. The FFA level of the pretreated brown grease was determined and an additional catalyst amount was calculated for neutralization. The total

Table 5.42: The changes in the acid values of the brown grease with 39.6% FFA in the pretreatment reaction with 10% sulfuric acid

	Methanol Molar Ratio	**Run 1**	**Run 2**
		A.V. (mg KOH/g)	*A.V. (mg KOH/g)*
After 1st Step	20:1	6.96	6.84
After 2nd Step	40:1	1.54	1.62

Table 5.43: Ingredient amounts for transesterification of pretreated brown grease for one batch

Reactant	*Amount (kg)*
Pretreated Brown Grease	180
Methanol	23.58
$NaOCH_3$ (0.21%)	0.23
$NaOCH_3$ (to neutralize)	0.45

catalyst amount is also shown in the table. After pretreatment, the process was continued with the alkaline catalyst (0.21% $NaOCH_3$ + neutralization amount) at a 6:1 molar ratio of methanol. The molar ratio of alcohol and the catalyst amount were calculated for the transesterification based on the initial amount of oil in the brown grease. The transesterification process was conducted at room temperature for 8 hours. Then, the mixture was pumped to the separation tank, and the ester and glycerin layers were allowed to separate in the tank overnight. A sample was taken from the bottom of the separation tank and it was washed with hot water. After settling the mixture, it was observed that the material that had collected at the bottom of the tank contained same ester. Therefore, it was determined that the separation did not occur completely. The mixture was washed six times for 30 minutes 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 extracting the wash water-glycerin mixture, the ester was pumped to the storage tank. After the 4th washing step the interphase material that had accumulated between the ester and wash water was separated from the ester. The reaction completion data for the brown grease after reaction with the alkaline catalyst are shown in Table 5.44 for two separate runs.

The acid values measured in the large-scale biodiesel production from brown grease were very close to those from the laboratory-scale biodiesel production from brown grease. The 2-step pretreatment with 10% sulfuric acid was successful for the pilot plant-scale biodiesel production from brown grease with 39.6% FFA in the same way as it had worked on the laboratory scale. This confirms that the sulfuric acid amount has a strong effect on the reduction of the acid level of feedstocks with high FFAs. After the transesterification of the brown grease, the results confirmed that more catalyst used in the transesterification reaction increased the soap formation and reduced the ester yield. The glycerin separation problem continued even though the sodium methoxide was used at a concentration as low as 0.21%.

Table 5.44: Transesterification reaction of the brown grease with 39.6% FFA

Run No.	*Catalyst Amount (%)*	*Total Glycerin (%)*	*Free Glycerin (%)*	*Specific Gravity*	*Yield (%)*
1	0.41	0.20	0.0103	0.8747	63.81
2	0.21	0.20	0.0185	0.8749	73.88

5.7.6. 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. Three different methyl esters were produced from soybean oil, yellow grease with 9% FFA, and brown grease with 39.6% FFA as described in the three case studies discussed earlier. The percentage and amounts of soap and catalyst in the ester, wash water, and glycerin are shown in Table 5.45. Table 5.46 shows the catalyst metal mass balance. 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 wash water due to the lack of glycerin separation. Almost all of the catalyst was removed with the first 2 wash water cycles. No catalyst was found in the wash water after the 2nd washing but soap was still found in the following washing steps. The total amounts of potassium (K) output and sodium (Na) output were very close to the input amount. This confirms the accuracy of the measurements and that most of the catalyst and soap were removed from the biodiesel. As was seen in the Table 5.45, the washing of yellow and brown grease is incomplete yet the Na balance shows that very little soap remains. Also, The interphase was not analyzed but the Na balance indicates that it cannot contain much Na. Therefore, it is probably not a soap compound.

Table 5.45: Analysis of the catalyst amount and soap produced in the pilot plant transesterification reaction

Sample	***Soybean Oil****		***Yellow Grease*****		***Brown Grease*****	
	% 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	-	-	-	-

* KOH was used as an alkaline catalyst.

** $NaOCH_3$ was used as an alkaline catalyst.

Table 5.46: 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	**1143.30 g K**	**389.38 g Na**	**289.37 g Na**
Methyl Ester	3.082 g	1.047	1.2904
Glycerin	1076.41 g	-	-
Wash Water	56.82 g	386.59	290.37
Total output of Pure Metal Catalyst	**1136.31 g K**	**387.64 g Na**	**291.66 g Na**

5.7.7. Summary of the Pilot Plant Operation and Analysis

The main objective of this study was to develop procedures to prepare large amounts of methyl esters from soybean oil, yellow grease, and brown grease with high FFA using the pilot plant. To prepare biodiesel from soybean oil, 1% KOH was used as the catalyst with methanol at a 6:1 molar ratio. The transesterification reaction was conducted at room temperature for 8 hours. For yellow grease and brown grease, the 2-step acid-catalyzed pretreatment reaction developed in the earlier part of the project was applied to reduce its acid value to less than 2 mg KOH/g. Then, the transesterification reaction was continued with 0.21% sodium methoxide as the alkaline catalyst at room temperature for 8 hours.

The following conclusions can be drawn from the pilot plant-scale biodiesel production from soybean oil, yellow grease, and brown grease with high FFA.

1. The mixing process is very important in determining the completeness of the transesterification reaction and the product yield.
2. The two-step acid catalysis process was successful in decreasing the acid values of the yellow grease and brown grease to less than 2 mg KOH/g. However, the brown grease required 10% catalyst in the 2-step pretreatment reaction. After decreasing the acid value of the feedstocks, alkaline catalyst transesterification gave good ester conversion and

biodiesels met the total and free glycerin specification.

3. After transesterification of the pretreated yellow and brown grease, the glycerin did not separate after overnight settling.
4. The number of washing cycles is very important and affects the total and free glycerin amount in the ester produced from pretreated feedstocks with high FFA. When the number of washing cycles was increased from 4 to 6, the total glycerin and free glycerin amount in the ester decreased from 0.29% to 0.23% and from 0.124% to 0.019%, respectively.

5.8. Economic Analysis of the Methyl Esters Produced in the Pilot Plant

An economic analysis of the methyl esters produced in the pilot plant was conducted for a 50-gallon batch of biodiesel production. The costs for producing biodiesel from feedstocks with high FFA and from soybean oil are presented.

5.8.1. Cost Analysis of the Methyl Esters Produced in the Pilot Plant

In the cost analysis, only the operating cost was estimated. The capital cost was not included. However, the capital cost for the pilot plant that process yellow and brown grease will be somewhat higher than for soybean oil because of the need for pretreatment equipment. The 12 month average prices [99] of the feedstocks and chemicals were taken as a base since the change in the prices of the feedstocks and chemicals will affect the biodiesel cost. In addition, to investigate the sensitivity of the operating cost to variations in the feedstock costs, three market prices, a minimum, an average, and a maximum price, were used by estimating from the annual market average price variations over the last 5 years [100, 74]. These prices are shown in Tables 5.47 and 5.48.

Table 5.47: Market prices of soybean oil and yellow grease in last 5 years

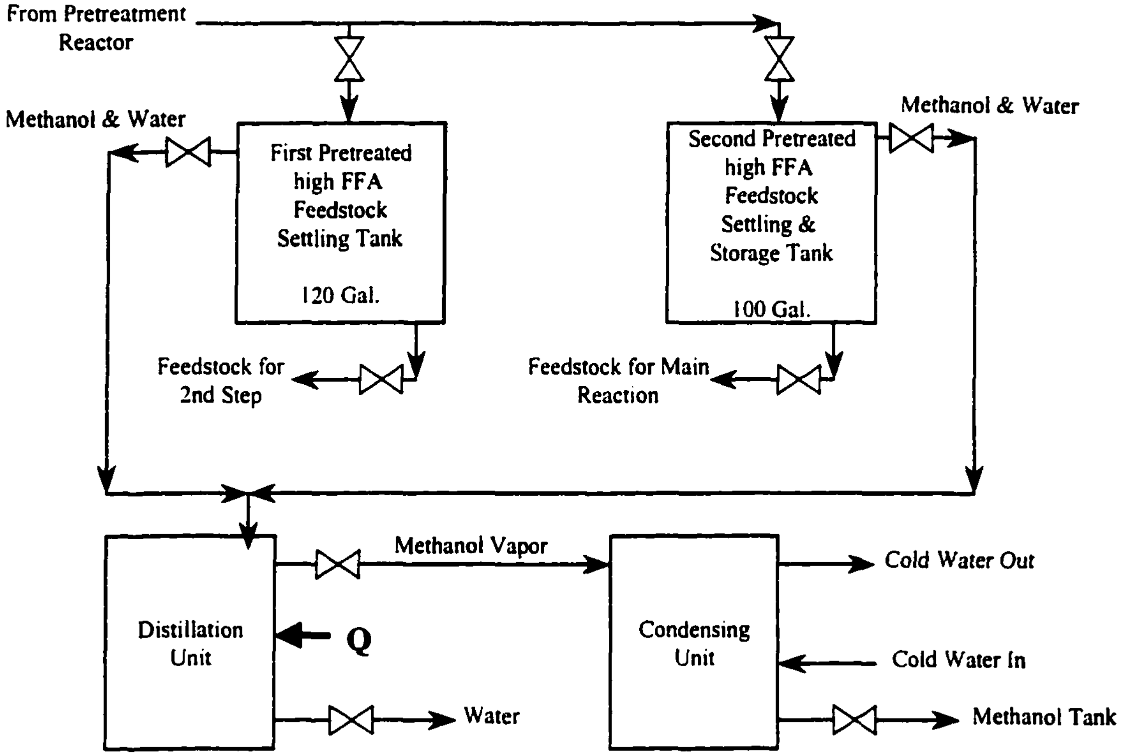
Marketing Year	*Soybean Oil ($/lb)*	*Yellow Grease ($/lb)*
1995	0.247	0.1476
1996	0.225	0.1600
1997	0.258	0.1465
1998	0.199	0.1141
1999	0.157	0.0938

Table 5.48: Market prices of the feedstocks and chemicals used in the calculation

Feedstock/Chemical	*Minimum*	*Average*	*Maximum*
Soybean Oil ($/lb)	0.15	0.20	0.25
Yellow Grease ($/lb)	0.08	0.13	0.18
Brown Grease ($/lb)	0.05	0.09	0.13
Methanol ($/gal)	0.35	0.40	0.45
Sulfuric Acid ($/ton)	41.00	46.00	51.00
Sodium Methoxide ($/lb)	0.60	0.65	0.70

In the cost analysis, glycerin recovery has not been included because the clean-up costs are still uncertain but the value of the glycerin will partially off set the capital costs of the equipment. However, it was assumed that the excess methanol used in the pretreatment and transesterification reactions was recovered. A methanol recovery diagram is shown in Figure 5.25. Although this equipment is not currently installed on the pilot plant, it will be installed in the future. Natural gas was assumed to be used for the heating processes and 80% efficiency was assumed. Two separate recovery units were assumed. Since the methanol recovery process in the pretreatment unit contains some water, it requires another distillation unit to separate the methanol from the water. Therefore, the main reaction recovery unit was separated from the pretreatment recovery unit. In the main unit the recovery of methanol was assumed to occur after the transesterification. Then, it was assumed the mixture will be allowed to settle overnight to separate the methyl ester from the glycerin. It was expected that this type of recovery will save energy and reduce the operating cost. Other operating costs,

Methanol Recovery in Pretreatment Unit



Methanol Recovery in Main Unit

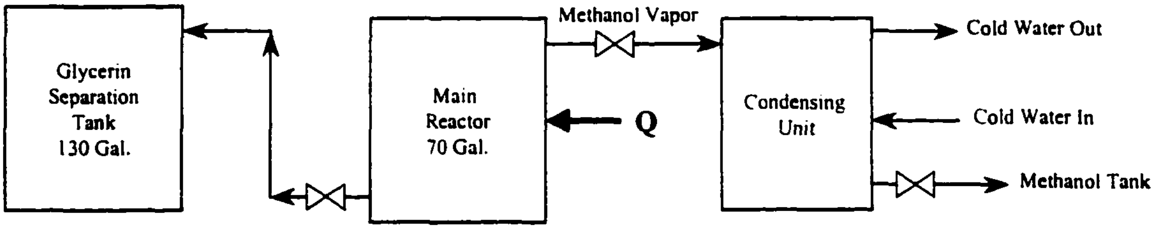


Figure 5.25: Methanol recovery diagram

Table 5.49: Utility costs for biodiesel production

Type of Cost	*Cost Amount*
Natural Gas ($/1000 ft^3)	3.34
Electrical ($/kW-hr)	0.062
Water ($/100 ft^3)	1.39

such as the natural gas price for the methanol recovery, electrical, and water costs were included to determine the final biodiesel price. Table 5.49 shows these utility prices.

5.8.2. 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 5.50. The calculation is based on the estimated average price for the yellow grease. The pump used in the first step of pretreatment to transfer the feedstock and for 1 hour of recirculation had a 0.373 kW maximum power requirement and the heater had 3 kW of power. The pump was used for 1.5 hours 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 minutes 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

Table 5.50: A sample cost calculation of yellow grease biodiesel

Cost Type	*Amount*	*Unit Cost*	*Cost ($)*	*Explanation*
Yellow Grease	20 kg	0.2865 $/kg	**5.7304**	feedstock cost
For 1st step pretreatment				
Methanol	0.225 kg	0.137 $/kg	0.031	stoichiometric
Catalyst (sulfuric acid)	0.09 kg	0.101 $/kg	0.0091	5% based on FFA amount
Electricity (for pumping)	1.5 hours	0.062 $/kW-hr	0.035	0.373 kW pump power
Natural Gas (for heating)	24.5 kg mixture	0.167 $/kg (natural gas)	0.069	-
4.275 kg Methanol recovery	0.128 kg natural gas required	0.167 $/kg (natural gas)	0.021	the excess methanol was recovered
For 2nd step pretreatment				
Methanol	0.053 kg	0.137 $/kg	0.0073	stoichiometric
Catalyst (sulfuric acid)	0.021 kg	0.101 $/kg	0.0021	5% based on FFA amount
Electricity (for pumping)	1.5 hours	0.062 $/kW-hr	0.035	0.373 kW pump power
Natural Gas (for heating)	22.13 kg mixture	0.167 $/kg (natural gas)	0.064	-
2.077 kg Methanol recovery	0.062 kg natural gas required	0.167 $/kg (natural gas)	0.010	the excess methanol was recovered
Total for pretreatment of 20 kg feedstock =			**5.9919**	for one process
Total for pretreatment of 180 kg feedstock =			**53.9271**	for nine process
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 hours	0.062 $/kW-hr	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	0.481kg natural gas required	0.167 $/kg (natural gas)	0.081	the excess methanol was recovered
Total for transesterification of 180 kg feedstock =			**4.9174**	for one process
Total overall cost =			**58.8445**	for one batch
Unit Costs =	***0.3592 $/kg***	***0.1630 $/lb***	***1.1739 $/gal***	for 91% yield

for 8 hours also had 0.373 kW maximum power. The pumping time for the feedstock into and out of the main reactor was assumed to be 2 hours and the pump was used for another 2 hours in the washing process. Thus, the 0.373kW pump was on for a total of 12 hours during the reaction giving a total of 4.78 kW-hrs of electrical power required.

The biodiesel cost comparisons are presented in Table 5.51 and in Figures 5.26, 5.27, and 5.28 for the minimum, average, and maximum consumable prices, respectively. Table 5.51 shows the cost for the fuels considered in the three case studies and the figures show the costs for various values of the FFA level. As seen in the figures, the FFA level of the feedstock affects the operating cost slightly. As mentioned earlier, the methanol amount increases in the pretreatment process of the feedstock with higher FFA. This 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 FFA by a large amount.

The costs to produce biodiesel from soybean oil, yellow grease with 9% FFA, and brown grease with 40% FFA are similar to each other. When compared on this basis the consumable costs for the biodiesels from both YGME and BGME are considerably less than for SME because of their lower feedstock cost. Even if the yield was assumed to be only 91% for both the YGME and BGME, their costs were still lower than for SME. State and federal excise taxes on diesel fuel used for on-highway trucks are $0.225/gallon and $0.244/gallon, respectively. When these are added to the $0.911 cost of biodiesel from brown grease and a 12% penalty is charged to the biodiesel due to its lower energy content, the cost per gallon for BGME biodiesel is $1.55. While this cost does not include the capital cost of the plant or transportation and profit, it is close to current diesel fuel prices.

Table 5.51: Cost comparison of the methyl esters produced in the pilot plant

Cost Type (\$/gal)	*Type of Methyl Ester*		
	(if yield 99%)		
	SME	YGME	BGME
Minimum	1.206	0.721	0.526
Average	1.584	1.103	0.837
Maximum	1.962	1.485	1.148
	(if yield 91%)		
Minimum	-	0.761	0.573
Average	-	1.177	0.911
Maximum	-	1.592	1.248

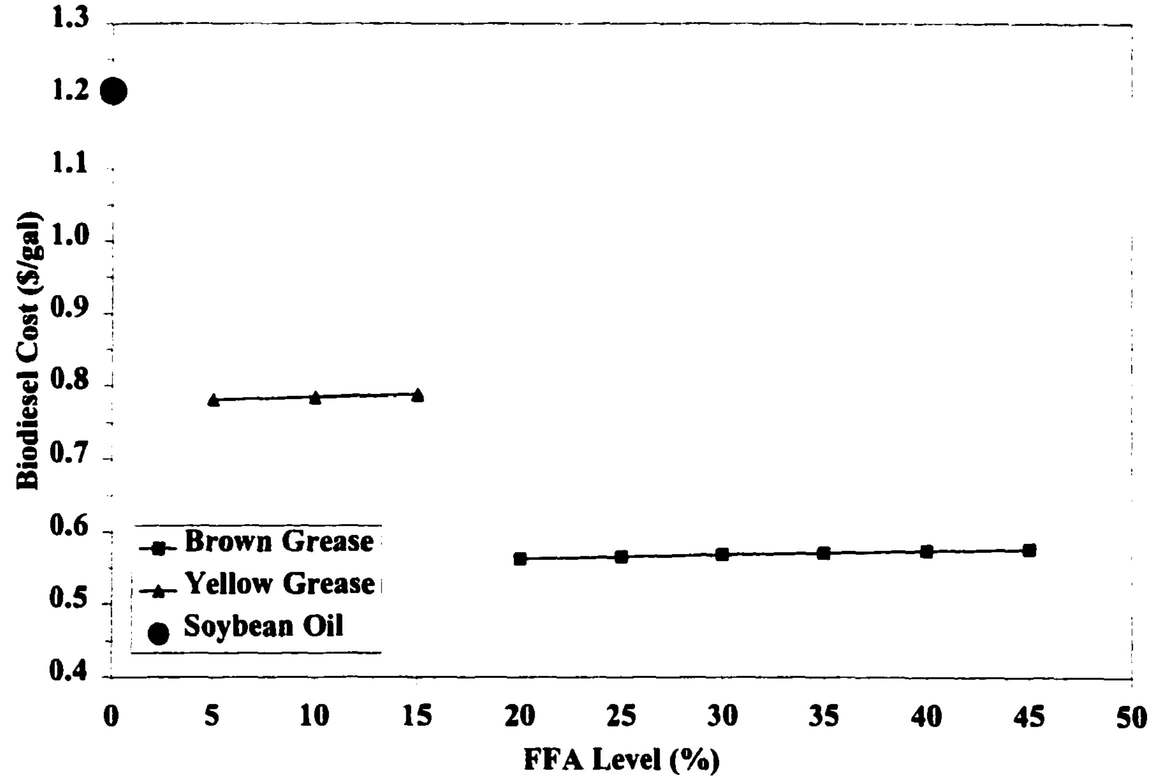


Figure 5.26: Biodiesels cost comparison at minimum consumable prices

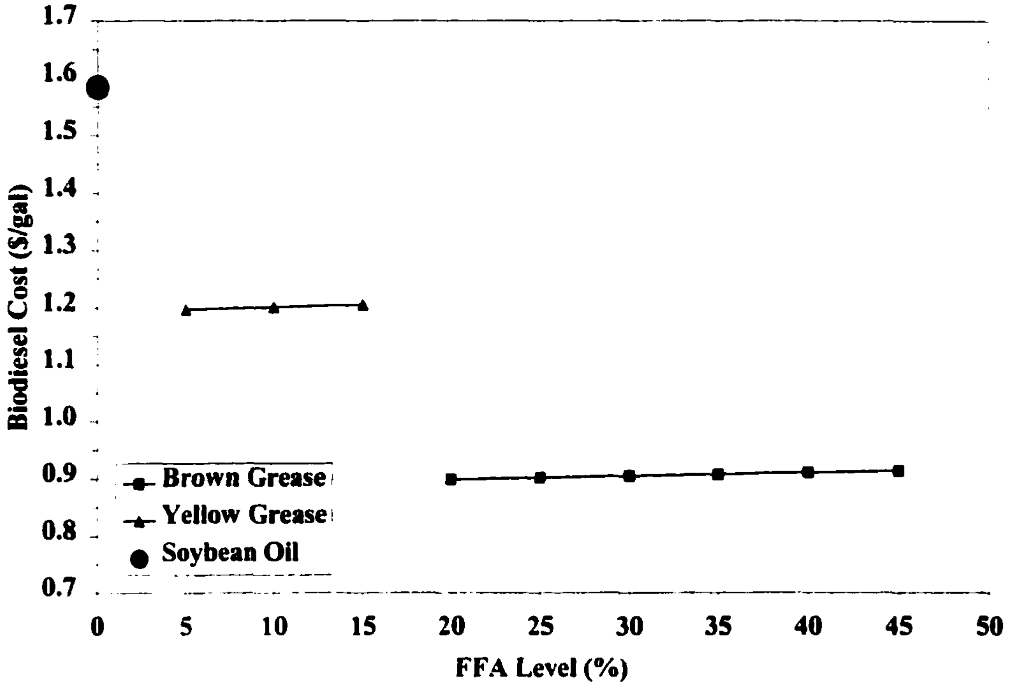


Figure 5.27: Biodiesels cost comparison at average consumable prices

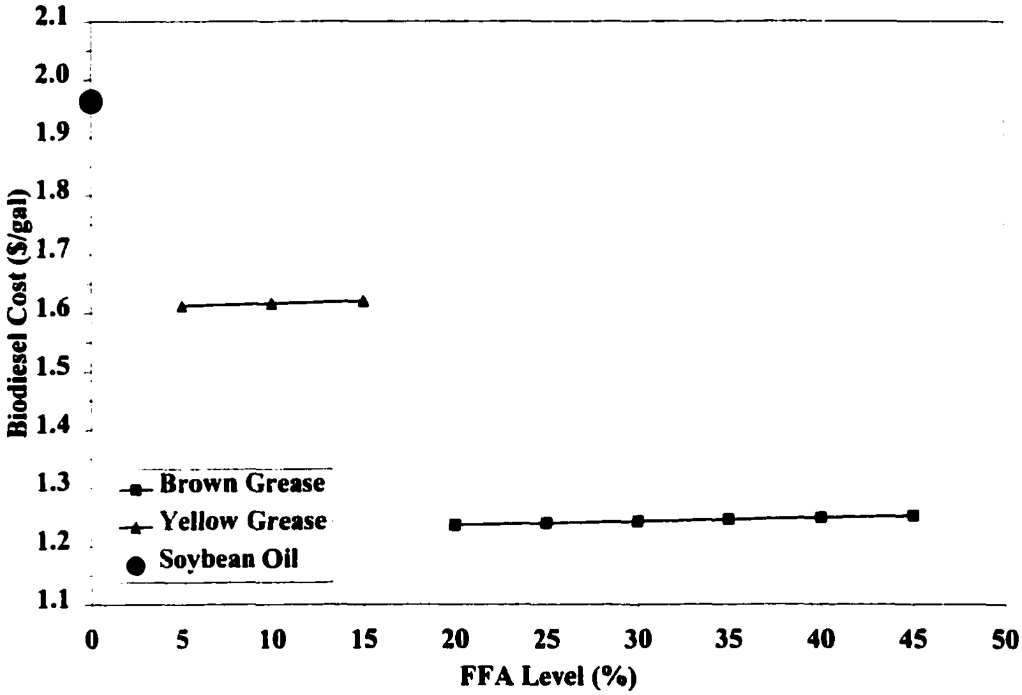


Figure 5.28: Biodiesels cost comparison at maximum consumable prices

6. ENGINE TEST RESULTS AND DISCUSSION

This chapter discusses the engine performance and emissions of a diesel engine fueled with No. 2 diesel fuel, yellow grease methyl esters (YGME), soybean oil methyl esters (SME), a 20% YGME blend in No. 2 diesel fuel, and a 20% SME blend in No. 2 diesel fuel. Each engine test was repeated three times. The average of the three data points was used in the figures and the error bars show the spread between maximum and minimum points among the three values. The raw data collected during the engine test are provided in Appendix G.

The first section will present the fuel property data and then the engine performance and emission data will be discussed.

6.1. Properties of the Fuels Used in Engine Test

This section presents the physical and chemical properties of the fuels used in the engine test. The No. 2 diesel fuel was purchased from a commercial supplier. Soybean oil methyl ester and yellow grease methyl ester were prepared in the pilot plant located at the BECON facilities of the Iowa Energy Center in Nevada, Iowa. The fatty acid compositions of the feedstocks and their esters are shown in Table 6.1. It was observed that the total saturated fatty acid composition of the yellow grease was 39.76% and the saturated fatty acid composition of the soybean oil was 16.29%. Palmitic (C16:0) and stearic (C18:0) acids were the most common saturated fatty acids in the yellow grease at 23.24% and 12.96%, respectively. As seen in Table 6.1, after transesterification, the saturated fatty acid percentages in the ester remained almost the same when compared with the respective feedstock. This confirms the earlier observation that saturation level does not affect the transesterification reaction.

The physical and chemical properties of the No. 2 diesel fuel, soybean oil methyl ester, and yellow grease methyl ester are presented in Table 6.2. When compared with No. 2 diesel fuel, the methyl esters from soybean oil and yellow grease contain around 11% O_2. However, the C/H ratios are lower than that of the No. 2 diesel fuel. The sulfur contents of the esters were less than the measurement threshold of 0.005%, while the diesel fuel used in this study contained 0.041% sulfur. The gross heat of combustion of the methyl esters from soybean oil and yellow grease were 39,871 kJ/kg and 39,817 kJ/kg, respectively, which were 12% lower than the 45,339 kJ/kg gross heat of combustion of the diesel fuel. The calculated molecular weights of the esters from soybean oil and yellow grease were 291.62 and 283.52, respectively, which were 50% and 46% higher than the 193.89 estimated molecular weight of the diesel fuel. The cetane number of the esters from soybean oil and yellow grease were 51.5 and 62.6, respectively, which were 21% and 47% higher than the 42.6 cetane number of the diesel fuel. However, both esters had higher specific gravity and kinematic viscosity

Table 6.1: Fatty acid composition of the feedstocks and the esters

Product	***Carbon Chain (%)****										***Unknown Components***	***Sat. (%)***
	C14:0	**C15:0**	**C16:0**	**C16:1**	**C17:0**	**C18:0**	**C18:1**	**C18:2**	**C18:3**	**C20:0**		
Soybean Oil	<0.10	<0.10	10.58	<0.10	0.11	4.76	22.52	52.34	8.19	0.36	0.48	16.29
Soybean Oil Methyl Ester	<0.10	<0.10	10.56	<0.10	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

*Measured by Woodson-Tenent Laboratories, Inc., Des Moines, IA.

Table 6.2: The physical and chemical properties of No. 2 diesel fuel, soybean oil methyl ester, and yellow grease methyl ester

Test Property	*No. 2 Diesel Fuel*	*Soybean Oil Methyl Ester*	*Yellow Grease Methyl Ester*
Carbon (% mass)	86.70[a]	77.10[e]	76.46[e]
Hydrogen (% mass)	12.71[a]	11.81[e]	12.25[e]
Oxygen (% mass)	-	10.97[e]	11.29[e]
C/H Ratio	6.82	6.53	6.24
Sulfur (% mass)	0.041[a]	<0.005[a]	<0.005[a]
Typical Formula	$C_{14.09}H_{24.78}$[e]	$C_{18.74}H_{34.43}O_2$[e]	$C_{18.06}H_{34.72}O_2$[e]
Average Molecular Weight	193.89[d]	291.62[e]	283.52[e]
Cetane Number (ASTM D613)	42.6[a]	51.5[a]	62.6[a]
Gross Heat of Combustion (kJ/kg)	45,339[a]	39,871[a]	39,817[a]
Net Heat of Combustion (kJ/kg)	42,640[a]	37,388[a]	37,144[a]
Specific Gravity (mm^2/s @ 21°C)	0.8537[c]	0.8814[c]	0.8728[c]
Kinematic Viscosity (@ 40°C, mm^2/s)	2.8271[c]	4.2691[c]	5.1643[c]
Total Glycerin (%)	-	0.028[b]	0.129[b]
Free Glycerin (%)	-	0.000[b]	0.015[b]
Distillation (ASTM D86, °F)[a]			
Initial Boiling Point	352	-	-
5%	392	-	-
10%	413	-	-
20%	440	-	-
30%	462	-	-
40%	482	-	-
50%	502	-	-
60%	522	-	-
70%	543	-	-
80%	569	-	-
90%	602	-	-
95%	630	-	-
End Point	653	-	-
Recovery (%)	98.0	-	-
Residue (%)	1.9	-	-
Loss (%)	0.1	-	-

[a] Measured by Phoenix Chemical Laboratory Inc., Chicago, IL.

[b] Measured by Williams Laboratory Services, Kansas City, KS.

[c] Done in Department of Mechanical Engineering, Iowa State University, Ames, IA.

[d] Calculated using Universal Oil Products Method 375-86, Des Plaines IL.

[e] Calculated from Fatty Acid Distribution.

when compared with the diesel fuel. The total and free glycerin amount in the esters, which were 0.028% and 0.000%, and 0.129% and 0.015%, respectively, for the soybean oil methyl ester and yellow grease methyl ester, met the ASTM specifications (ASTM PS121) for biodiesel.

6.2. Performance and Emissions of the Diesel Engine Fueled with Biodiesel

This section will discuss the diesel engine emissions and performance when the engine was fueled with biodiesel from yellow grease, soybean oil, and No. 2 diesel fuel.

6.2.1. Engine Performance

In order to understand the effect of the biodiesel on the engine performance and emissions, the brake specific fuel consumption (BSFC), in g/kW-hr, and thermal efficiency of the engine were measured at full load (190 ft-lbf) and at an engine speed of 1400 rpm. The engine load and speed were kept constant for all of the test fuels. Therefore, the brake power was kept constant throughout the tests.

A statistical analysis technique called "Tukey Grouping" was performed on the data. This technique provides specific information on the interaction between the variables. If the variables in the Tukey Grouping have the same letter this means the differences between those variables are not statistically significant. The Tukey Grouping analysis for the BSFC is shown in Table 6.3. From this table, it was concluded that there was no significant difference between the BSFC of the engine operating on SME and YGME, and between the 20% blend of SME and the 20% blend of YGME. However, both biodiesels and their blends have a significant effect on the BSFC compared with the No. 2 diesel fuel.

Table 6.3: Tukey's Studentized range (HSD) test for BSFC

Tukey Grouping	Mean	N	FUEL
A	260.9367	3	SME
A	259.3267	3	YGME
B	234.5533	3	20% YGME
B	234.2867	3	20% SME
C	228.4167	3	No. 2 Diesel

Minimum Significant Difference = 2.7884

Analysis of variance (ANOVA) was also conducted to determine the level of significance of the different fuels on the engine performance and emissions, and the complete analysis results are shown in Appendix F. In the ANOVA tables, DF represents the degrees of freedom, the F value represents the probability distribution in repeated sampling, and Pr represents the weight of the significance. When the value shown in the Pr > F column is small (approximately 0.0001) then the significance of the difference between the fuels is large. The significance level (Pr > F value) of the fuels on the dependent variable can be identified from the ANOVA tables. For all of the statistical analyses of this study, a 95% confidence interval was used. The R-squared value and the mean of the dependent variable are also shown in the ANOVA table. The results of the ANOVA for the brake specific fuel consumption (BSFC) are shown in Table 6.4. Since the Pr value is 0.0001 in the ANOVA table, the fuels tested in the engine have a significant effect on the BSFC.

Table 6.4: Analysis of variance (ANOVA) for BSFC

Dependent Variable: BSFC

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
FUEL	4	2840.868	710.217	659.58	0.0001
Error	10	10.768	1.077		
Corrected Total	14	2851.636			

R-Squared = 0.9962; BSFC Mean = 243.504

For each fuel type, the BSFC and the percentage change in the BSFC are shown in Figures 6.1 and 6.2, respectively. Table 6.5 also summarizes the average values measured and the percent changes for the fuels used in the engine tests. As seen in the table and figures, the methyl esters have higher BSFCs than the No. 2 diesel fuel. The increase in BSFC is understandable since the methyl esters had heating values that were about 12% less than for No. 2 diesel fuel.

Figure 6.2 shows the percent change in BSFC relative to No. 2 diesel fuel. The YGME had a 14.24% increase in BSFC when compared with No. 2 diesel fuel while the SME had a 13.53% increase. When the two esters are compared with each other, there was a 0.71% higher BSFC measured for the YGME. When looking at the blends, the 20% YGME

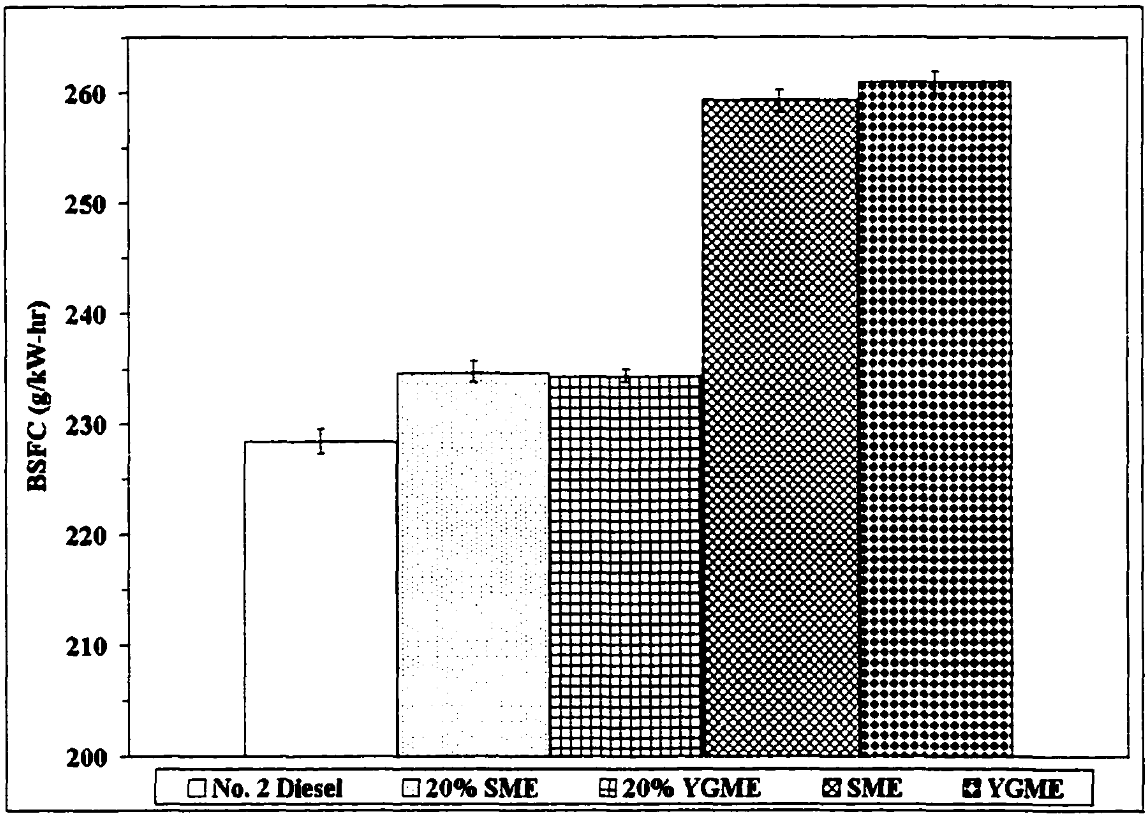


Figure 6.1: Comparison of brake specific fuel consumption (BSFC)

blend had a 2.57% increase and the 20% SME had a 2.69% increase in BSFC. These results are similar to those of Monyem [78], and McDonald et al. [101] who fueled a diesel engine with soybean oil methyl ester and No. 2 diesel fuel. In those studies, a 13 to 14 % increase in BSFC for the methyl esters was found. Ali [102] studied the effect of beef tallow methyl ester on engine performance and emissions. He also found a 12 to 14 % increase in BSFC which confirms the results given above.

The brake thermal efficiencies of the engine when operating on the different fuels and blends are shown in Figure 6.3. The brake thermal efficiency is defined as the actual brake work per cycle divided by the amount of fuel chemical energy as indicated by the fuel's lower heating value. As the figure shows, the thermal efficiency of the SME, YGME, and

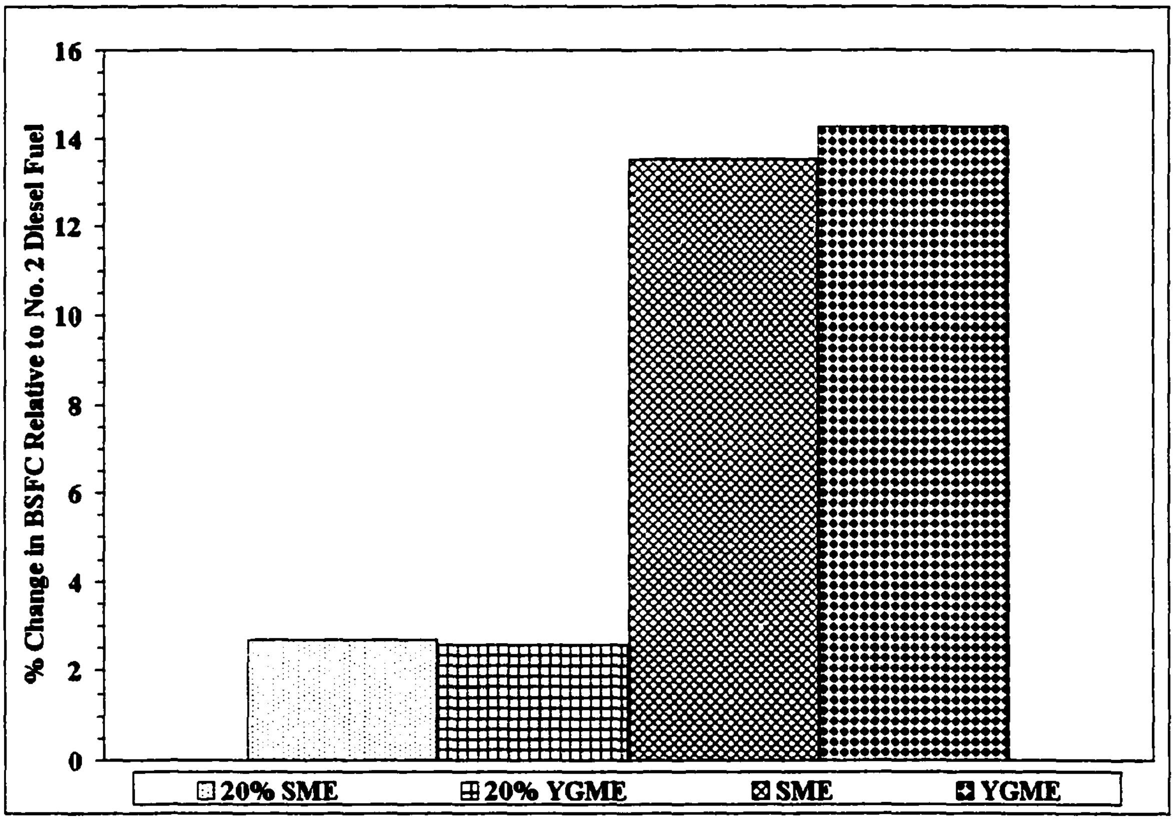


Figure 6.2: Percent change in BSFC

their blends were almost the same as for the No. 2 diesel fuel. This means that the engine converts the chemical energy of the fuel to mechanical energy with the same efficiency for all the fuels used in the test. The thermal efficiency for all of the tested fuels was about 37% at a load of 190 ft-lbf and an engine speed of 1400 rpm.

Table 6.5: Average values and % changes in BSFC and thermal efficiency

Fuel Type	*BSFC (g/kW-hr)*	*% Change in BSFC*	*Thermal Efficiency (%)*	*% Change in Thermal Efficiency*
No. 2 Diesel	228.42	-	36.96	-
20% SME	234.55	2.69	36.90	-0.16
20% YGME	234.29	2.57	36.99	0.07
SME	259.33	13.53	37.13	0.45
YGME	260.94	14.24	37.14	0.49

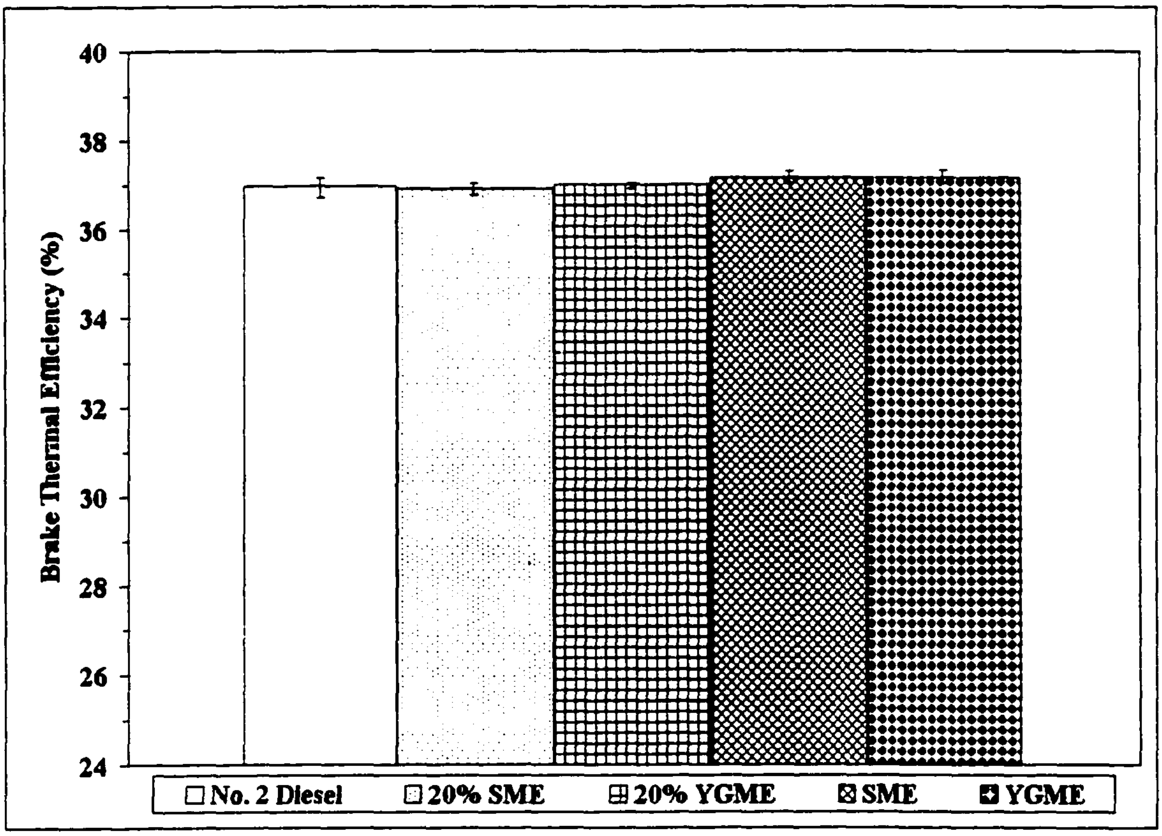


Figure 6.3: Brake Thermal efficiency at same engine condition

Monyem [78], Chang et al. [16], and Yahya [103] fueled a John Deere 4276T four-cylinder, four-stroke, turbocharged DI diesel engine with biodiesel fuels and No. 2 diesel fuel. They also found that the thermal efficiency of the biodiesel and their blends were the same as with No. 2 diesel fuel.

The results of the Tukey Grouping test for the thermal efficiency are shown in Table 6.6. From this table, it was concluded that there was no significant difference between the fuels since all of the fuels have same letter. The ANOVA analysis for the thermal efficiency is shown in Appendix F. The Pr value was much larger than 0.0001, which confirms that there was no significant difference between the thermal efficiency of the fuels.

Table 6.6: Tukey Grouping test for variable: Brake Thermal Efficiency

Tukey Grouping	Mean	N	FUEL
A	37.1433	3	SME
A	37.1300	3	YGME
A	36.9900	3	20% SME
A	36.9633	3	No. 2 Diesel
A	36.9033	3	20% YGME

Minimum Significant Difference = 0.4313

6.2.2. Engine Emissions

In this section, the exhaust emissions are discussed for YGME, SME, 20% YGME blend, 20% SME blend, and No. 2 diesel fuel at the load of 190 ft-lbf. and the engine speed of 1400 rpm. The exhaust emissions measured were carbon monoxide (CO), carbon dioxide (CO_2), unburned hydrocarbons (HC), oxides of nitrogen (NO_x), and the Bosch smoke number (SN). All results were converted to a brake specific basis (g/kW-hr) except for the SN. The values shown on the figures are the average of three data points and the error bars show the spread between the maximum and minimum points. The Tukey Grouping test table is also presented for each emission species.

6.2.2.1. Comparison of CO Emissions

Carbon monoxide (CO) in diesel engines is formed during the intermediate combustion stages. For fuel-rich mixtures such as are found in spark-ignited engines, CO concentrations in the exhaust increase steadily with increasing equivalence ratio as the amount of excess fuel increases. However, diesel engines always operate well on the lean side of stoichiometric. Therefore, CO emissions from the diesel engines are usually low and most engine manufacturers meet CO regulations easily [91].

The brake specific CO exhaust emissions are shown in Figure 6.4. For all of the methyl esters and blends, the CO emissions were less than for the No. 2 diesel fuel. Compared to No. 2 diesel fuel, the CO emissions of the SME and YGME were reduced by 18.22% and 17.77%, respectively. The CO emissions of the 20% blends of SME and YGME were decreased by 7.51% and 6.99%, respectively. Monyem [78], and Yahya [103] also found that biodiesel and their blends lowered CO emissions. In their study, they found 15.7% and 15.8% reductions in CO emissions compared to No. 2 diesel fuel, respectively, when the engine was fueled with neat biodiesel.

The Tukey Grouping test results for the BSCO are presented in Table 6.7. The analysis shows that there is a significant difference between the fuels. The ANOVA result in Appendix F also confirms these results. When the Tukey results for the neat biodiesels are compared to No. 2 diesel fuel, there is a significant difference. However, the table shows that no significant difference between the two neat biodiesels or between the two blends.

Table 6.7: Tukey Grouping test for variable: BSCO

Tukey Grouping	Mean	N	FUEL
A	0.55600	3	No. 2 Diesel
A	0.51700	3	20% SME
B A*	0.51400	3	20% YGME
C	0.45700	3	SME
C	0.45400	3	YGME

Minimum Significant Difference = 0.0406

* The Tukey analysis shows borderline significance with double letters

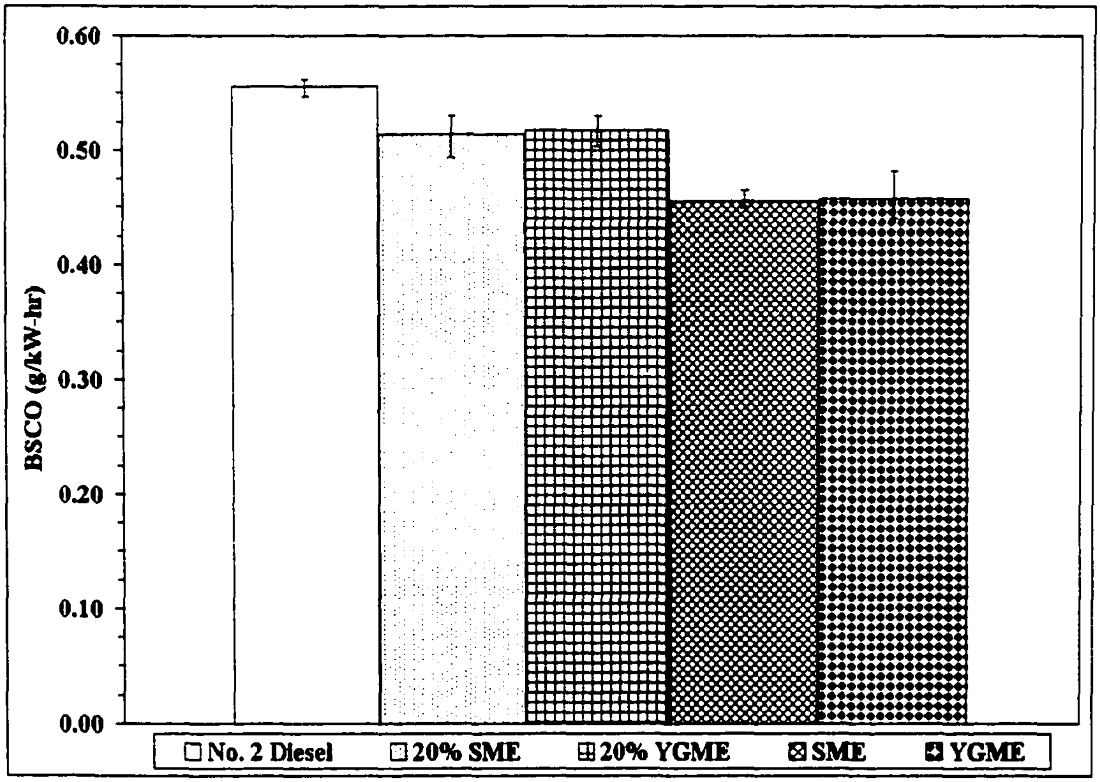


Figure 6.4: Comparison of the brake specific carbon monoxide (BSCO)

6.2.2.2. Comparison of CO_2 Emissions

Anything fueled by a carbon-based compound will produce carbon dioxide (CO_2) as one of its products. The brake specific CO_2 exhaust levels are shown in Figure 6.5. The CO_2 emissions for the methyl esters were only slightly higher than for the No. 2 diesel fuel.

Compared to No. 2 diesel fuel, the CO_2 emissions of the SME and YGME were increased by 1.78% and 1.15%, respectively. The CO_2 emissions of the 20% blends of SME and YGME were decreased by 0.04% and 0.06%, respectively. The changes of the CO_2 emissions from the methyl esters were very small compared to No. 2 diesel fuel and there was almost no difference in CO_2 emission observed between the two methyl ester blends and the No. 2 diesel fuel. Ali [102] and Yahya [103] also found no significant difference in CO_2 emissions between the biodiesel and No. 2 diesel fuel.

The Tukey Grouping analysis shown in Table 6.8 confirms that there is no significant difference between the fuels. All fuels have same letter in the table. The ANOVA analysis given in Appendix F also confirms these results.

Table 6.8: Tukey Grouping test for variable: $BSCO_2$

Tukey Grouping	Mean	N	FUEL
A	817.37	3	YGME
A	812.25	3	SME
A	803.02	3	No. 2 Diesel
A	802.70	3	20% YGME
A	802.56	3	20% SME

Minimum Significant Difference = 33.542

6.2.2.3. Comparison of Unburned HC Emissions

The unburned hydrocarbons are another emission product that is regulated by the Environmental Protection Agency. The amount of HC in the exhaust depends on the engine operating conditions, the fuel spray characteristics, and the interaction of the fuel spray with the air in the combustion chamber. The brake specific HC exhaust emissions are shown in Figure 6.6. For all of the methyl esters and blends, the HC emissions were less than for the

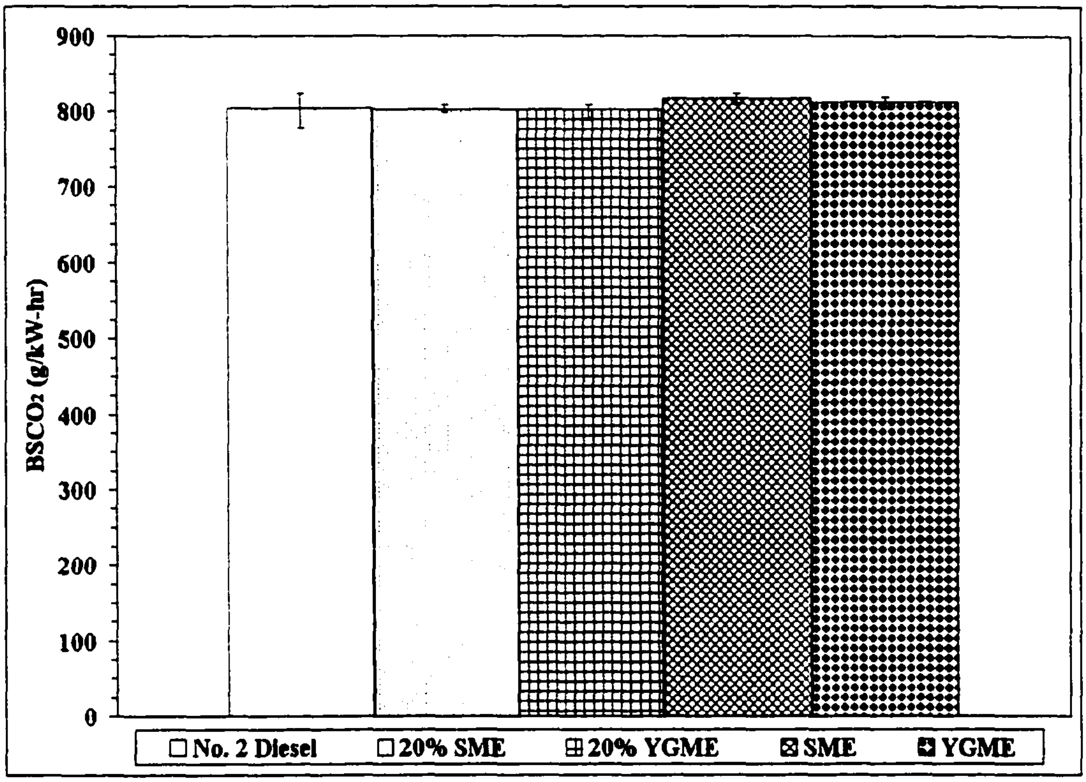


Figure 6.5: Comparison of the brake specific carbon dioxide ($BSCO_2$)

No. 2 diesel fuel. Compared with No. 2 diesel fuel, the highest HC reduction was found for YGME, which was 46.29%, while the SME has a reduction of 42.50%. The HC emissions of the 20% blends of SME and YGME were decreased by 3.05% and 2.27%, respectively. The differences between the methyl esters from different feedstocks appear to be much less than the differences between the esters and No. 2 diesel fuel. Monyem [78] and Chang et al. [16] also found significant HC reduction when biodiesel was used in the diesel engine.

The significance level for the change in BSHC is shown in Table 6.9. The table shows that there is a significant difference between the neat biodiesel fuels. However, the BSHC of the 20% blends of the biodiesels showed statistically similar results with No. 2 diesel fuel. The ANOVA table shown in Appendix F, also shows that the changes in the means of the BSHC emissions of the fuels were significant.

6.2.2.4. Comparison of NO_x Emissions

Oxides of nitrogen (NO_x) are another important emission product. While nitric oxide (NO) and nitrogen dioxide (NO_2) are usually grouped together as NO_x emissions, NO is the predominant oxide of nitrogen produced inside the engine cylinder.

Table 6.9: Tukey Grouping test for variable: BSHC

Tukey Grouping	Mean	N	FUEL
A	0.50300	3	No. 2 Diesel
A	0.49133	3	20% SME
A	0.48767	3	20% YGME
B	0.28900	3	YGME
B	0.27033	3	SME

Minimum Significant Difference = 0.0555

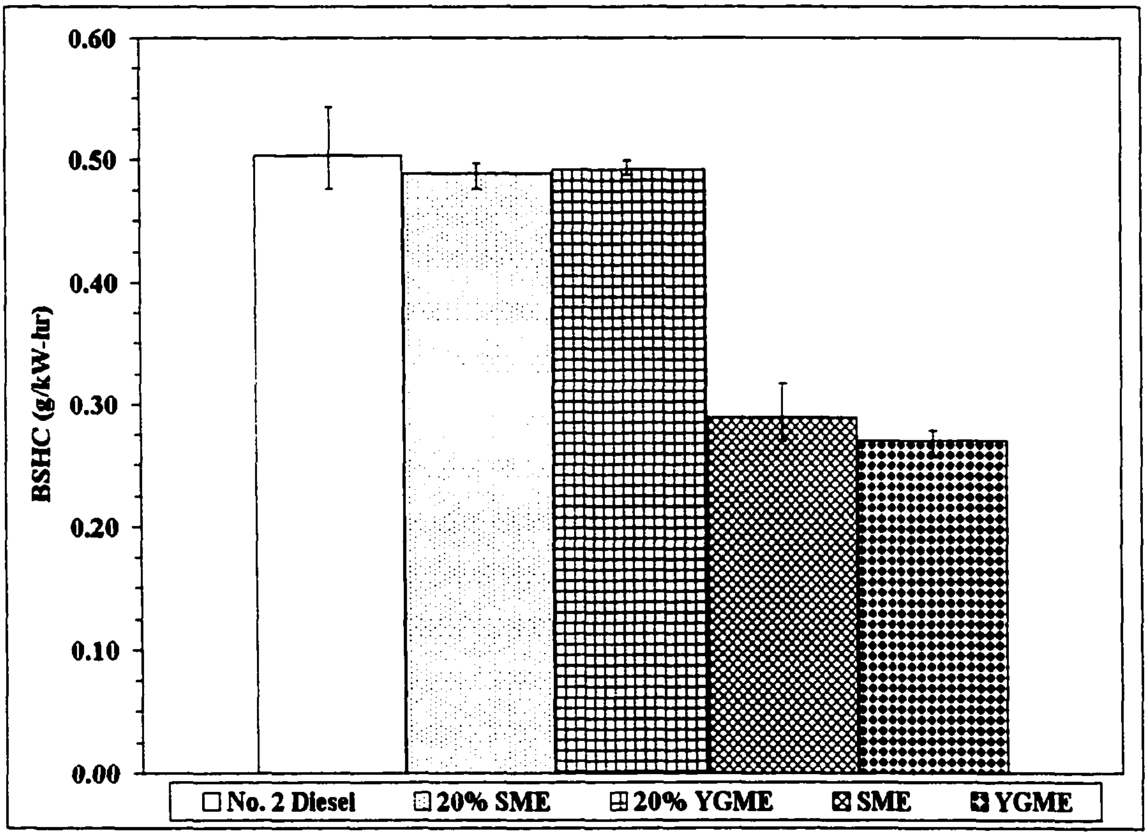


Figure 6.6: Comparison of the brake specific hydrocarbon (BSHC)

The brake specific NO_x exhaust emissions are shown in Figure 6.7. For all of the methyl esters, the NO_x emissions were higher than for the No. 2 diesel fuel. Compared with No. 2 diesel fuel, the NO_x emissions of the SME and YGME were increased by 13.09% and 11.6%, respectively. The NO_x emissions of the 20% blends of SME and YGME were increased by 1.51% and 1.14%, respectively. The NO_x increase in the emissions may be associated with the oxygen content of the methyl esters, since the fuel oxygen may provide additional oxygen for NO_x formation. However, the overall equivalence ratios for the methyl ester fuels were very similar to No. 2 diesel fuel. The impact of the fuel's physical properties on the engine's injection timing, which will be discussed later, is not fully understood but this may also play a role in the higher NO_x emissions.

Mittelbach and Tritthart [67] tested used frying oil methyl ester and they also found increased NO_x emissions compared to No. 2 diesel fuel. Rickeard et al. [104] and Monyem [78] also mentioned that the NO_x emission increased for the biodiesel fuels.

The neat fuels have a significant effect on the NO_x emissions as shown in Table 6.10. The Tukey Grouping shows that the NO_x emissions from the 20% blends were not significantly different from the No. 2 diesel fuel, but the neat fuels were significantly different from No. 2 diesel fuel.

Table 6.10: Tukey Grouping test for variable: $BSNO_x$

Tukey Grouping	Mean	N	FUEL
A	21.2753	3	YGME
A	20.9953	3	SME
B	19.0963	3	20% YGME
B	19.0273	3	20% SME
B	18.8130	3	No. 2 Diesel

Minimum Significant Difference = 0.5937

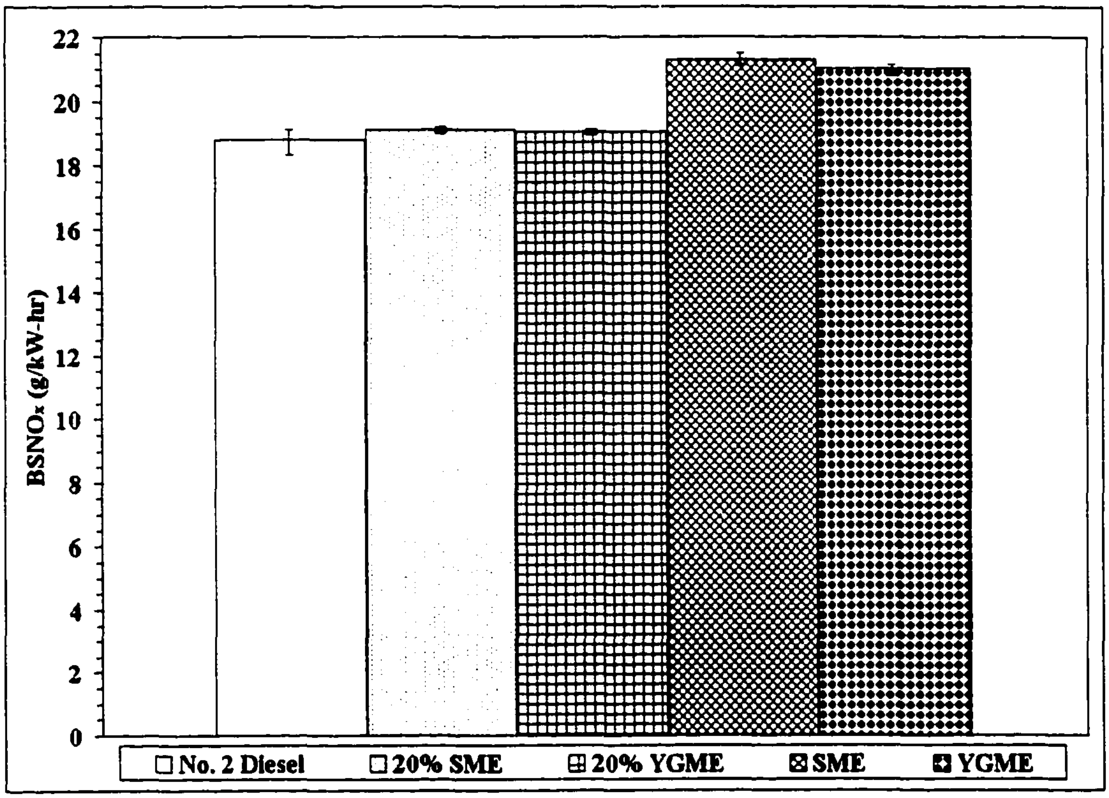


Figure 6.7: Comparison of the brake specific oxides of nitrogen ($BSNO_x$)

6.2.2.5. Comparison of Bosch Smoke Numbers (SN)

The Bosch smoke number (SN) data are shown in Figure 6.8. For all of the methyl esters and the blends, the SNs were less than for the No. 2 diesel fuel. The SNs of No. 2 diesel fuel, SME, and YGME were 1.06, 0.41, and 0.38, respectively. The smoke levels of the methyl esters and their blends were significantly lower than that of No. 2 diesel fuel. However, almost no difference was observed in the SNs between the two methyl esters and between the two blends.

Schumacher et al. [105] fueled a Dodge pickup with soybean oil methyl ester and found a large reduction (86%) in SN when using neat biodiesel. Monyem [78] found a 56.9% reduction in SN when fueling the engine with soybean oil methyl ester confirming the results of this study.

The statistical analysis for the SN is shown in Table 6.11 and Appendix F. The table shows that there are significant differences between the fuels. When the fuels are compared to each other, the Tukey Grouping shows that the neat biodiesels are significantly different from No. 2 diesel fuel. However, the blends show no significant difference compared to No. 2 diesel fuel at the 95% confidence level.

Table 6.11: Tukey Grouping test for variable: SN

Tukey Grouping	Mean	N	FUEL
A	1.05567	3	No. 2 Diesel
A	0.88900	3	20% YGME
A	0.87800	3	20% SME
B	0.41133	3	YGME
B	0.37767	3	SME

Minimum Significant Difference = 0.1865

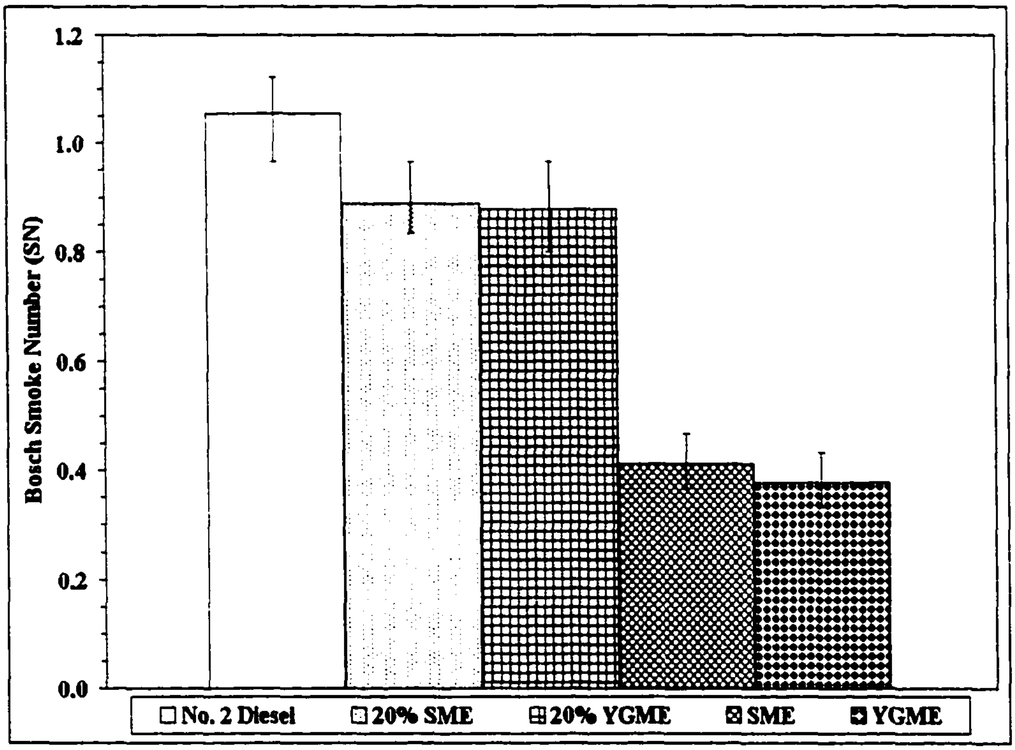


Figure 6.8: Comparison of the Bosch Smoke Numbers (SN)

6.2.2.6. Summary of Exhaust Emissions Results

A summary of the percent changes in the exhaust emissions compared to No. 2 diesel fuel is shown in Table 6.12 and Figure 6.9. A significant reduction was observed in CO, HC, and SN for YGME and SME. However, an increase in the NO_x emissions was found for both neat methyl esters. The emissions of CO, HC, and SN were reduced by 17.77%, 46.29%, and 64.21% for YGME, while SME had a reduction of 18.22%, 42.50%, and 61.05%, respectively. However, the increases in the NO_x emission were 11.60% and 13.09% for YGME and SME, respectively. The changes in CO_2 were not significant. The emissions of the methyl esters from the different feedstocks were very similar to each other.

Table 6.12: Average values and % changes in the engine emissions

Fuel Type	CO (g/kW-hr)	% Change in CO	CO_2 (g/kW-hr)	% Change in CO_2	HC (g/kW-hr)	% Change in HC	NO_x (g/kW-hr)	% Change in NO_x	SN	% Change in SN
No. 2 Diesel	0.56	-	803.0	-	0.50	-	18.8	-	1.06	-
20% SME	0.51	-7.51	802.7	-0.04	0.49	-3.05	19.1	1.51	0.89	-15.79
20% YGME	0.52	-6.99	802.6	-0.06	0.49	-2.29	19.0	1.14	0.88	-16.84
SME	0.45	-18.22	817.4	1.79	0.29	-42.50	21.3	13.09	0.41	-61.05
YGME	0.46	-17.77	812.3	1.15	0.27	-46.29	21.0	11.60	0.38	-64.21

6.3. Combustion Characteristics of the Fuels Tested in the Diesel Engine

This section will discuss the combustion characteristics of the fuels used in the engine tests. First, the timing for the start of fuel injection will be compared. Second, a comparison of the start of combustion and the fuel burning rate will be presented. Finally, the ignition delay will be discussed for the different fuels.

6.3.1. Comparison of the Start of Fuel Injection

The injection line pressure and start of fuel injection will be affected by changes in the fuel properties such as compressibility and speed of sound. The start of injection will also

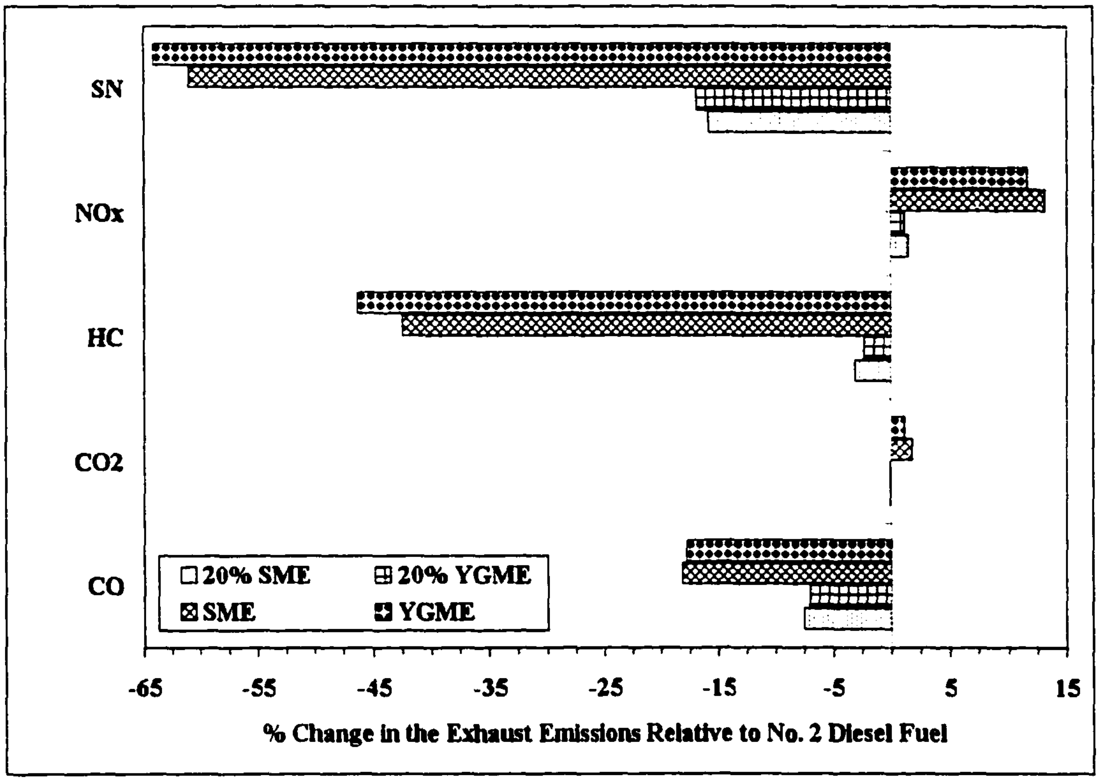


Figure 6.9: Percent change in the exhaust emissions relative to No. 2 diesel fuel

change due to changes in the fuel injection pump. Rotary fuel injection pumps of the type used on this engine have the property that their end of injection timing is fixed. When additional quantities of fuel are injected, the timing for the start of injection occurs earlier [106]. Since it was necessary to inject 13-14% more biodiesel to provide the same torque as with diesel fuel, the injection timing advanced several degrees.

The start of fuel injection for each fuel is shown in Table 6.13 and Figure 6.10. For the neat methyl esters, the start of fuel injection timings were earlier than for the No. 2 diesel fuel. The average starting timings for fuel injection for No. 2 diesel fuel, 20% SME, 20%YGME, SME, and YGME were 13.50°, 14.40°, 14.60°, 16.18°, and 17.05° BTDC, respectively. The start of fuel injection is usually taken as the time when the injector needle lifts off its seat. Since a needle lift sensor was not available for this study, the timing at which the fuel injection line pressure reached the injector nozzle opening pressure was taken as the start of injection. The injector nozzle opening pressure for the injectors used in the engine was about 207 bar.

The SME and YGME fuel both injected about 2.68° and 3.55° earlier than No. 2 diesel fuel, respectively. The blends had almost the same start of fuel injection. Figure 6.11

Table 6.13: Combustion characteristics of the fuels

Fuel	*Start of Fuel Injection (°BTDC)*	*Start of Combustion (°BTDC)*	*Ignition Delay (°)*
No. 2 Diesel	13.50	7.42	6.09
20% SME	14.40	8.33	6.07
20% YGME	14.60	8.50	6.10
SME	16.18	10.83	5.34
YGME	17.05	11.58	5.46

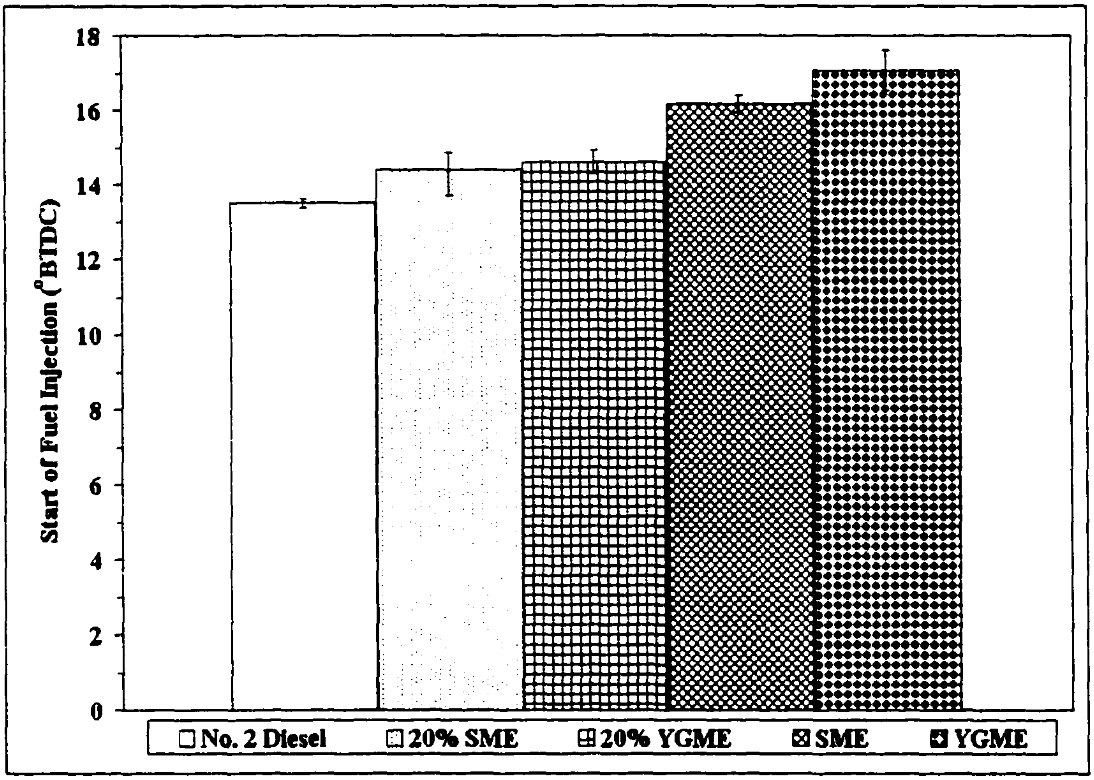


Figure 6.10: Start of fuel injection of the fuels

shows the injection line pressures for the fuels. Each fuel has a different injection line pressure since their physical fuel properties were different and different quantities of fuel were injected. The peak fuel injection pressure for the neat methyl esters was about 300 bars. Monyem [78] and Ali [102] obtained similar results, and they also mentioned that the start of fuel injection for biodiesel was earlier than for No. 2 diesel fuel.

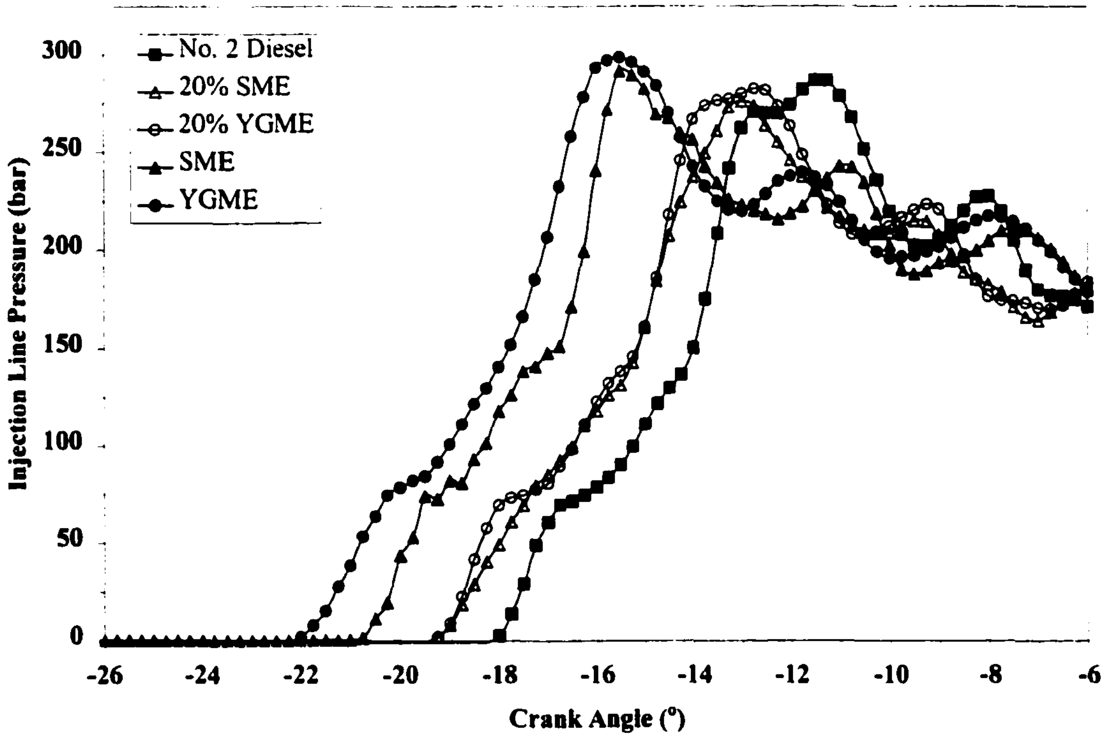


Figure 6.11: Injection line pressures of the fuels

The statistical results for the start of fuel injection are shown in Table 6.14. The table shows that the fuel type had a statistically significant effect on the start of fuel injection. However, the table also shows that there was no significant difference between the two methyl esters or between the two blends. The ANOVA table in Appendix F confirms the effect of different fuels on the start of injection.

Table 6.14: Tukey Grouping test for variable: Start of fuel injection

Tukey Grouping	Mean	N	FUEL
A	17.0467	3	SME
A	16.1767	3	YGME
B	14.5967	3	20% SME
C B	14.4033	3	20% YGME
C	13.5033	3	No. 2 Diesel

Minimum Significant Difference = 1.0885

6.3.2. Comparison of the Start of Combustion and Fuel Burning Rate

The chemical properties of the fuel will effect its combustion in the cylinder. One of the main properties is the cetane number of the fuel. The higher cetane number for biodiesel means the fuel is expected to ignite more readily and have a shorter ignition delay period.

In Table 6.13 and Figure 6.13, the starts of combustion timings for the fuels are shown. For the neat methyl esters, the start of combustion timings were earlier than for the No. 2 diesel fuel and this is confirmed by the heat release rate profiles shown in Figure 6.12. The start of combustion timings for No. 2 diesel fuel, 20% SME, 20%YGME, SME, and YGME were 7.42°, 8.33°, 8.50°, 10.83°, and 11.58° BTDC, respectively.

As described earlier, the start of combustion is affected by the cetane number of the fuel. Biodiesel has a higher cetane number than No. 2 diesel fuel. Therefore, it starts to burn earlier than the No. 2 diesel fuel. The SME and YGME fuel both started to burn about 3.4° and 4.2° earlier than No. 2 diesel fuel, respectively. The peak point in the heat release rate for the No. 2 diesel fuel was higher than for the neat biodiesels. Both methyl esters had significant differences in the start of combustion when compared to each other. The blends also had significant differences compared to No. 2 diesel fuel. Scholl et al. [3], Monyem [78], and Ali [102] found identical results in their studies.

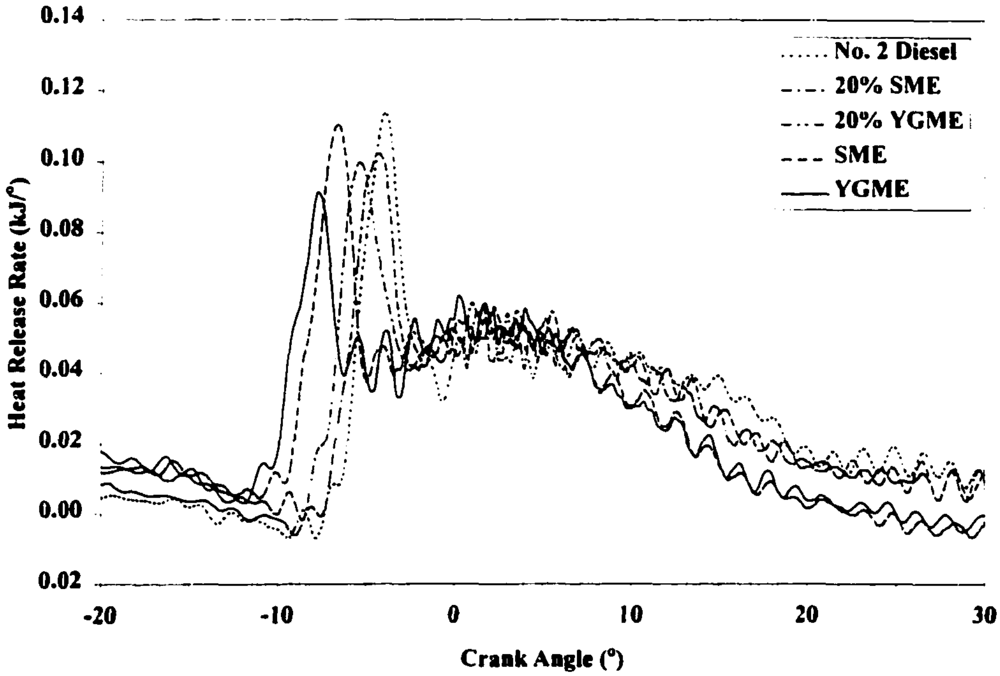


Figure 6.12: Heat release rate profiles of the fuels

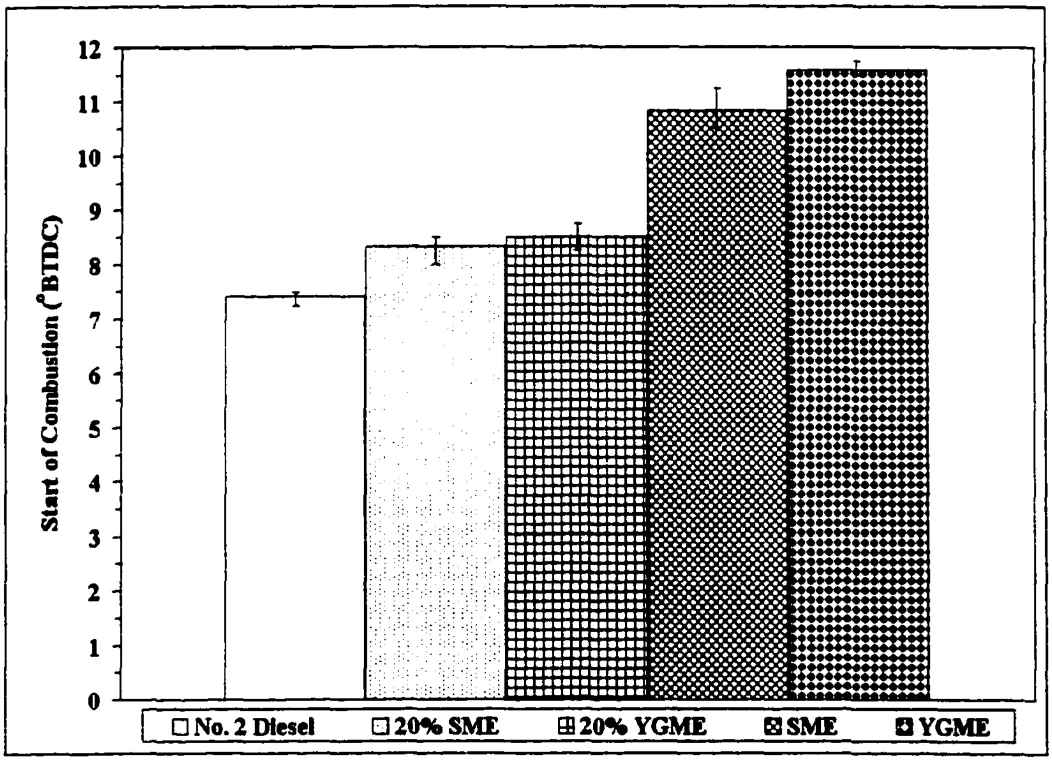


Figure 6.13: Start of combustion of the fuels

Table 6.15 shows the results of the statistical analysis for the start of combustion timings of the fuels. The ANOVA table in Appendix F also shows significant differences between the fuels. All fuels had statistically significant differences in the start of combustion compared to the base diesel fuel. If the two methyl esters were compared to each other, the table also shows that there was a significant difference between the neat esters but not between the two blends.

Table 6.15: Tukey Grouping test for variable: Start of combustion

Tukey Grouping	Mean	N	FUEL
A	11.5833	3	SME
B	10.8333	3	YGME
C	8.5000	3	20% SME
C	8.3333	3	20% YGME
D	7.4167	3	No. 2 Diesel

Minimum Significant Difference = 0.6938

6.3.3. Comparison of the Ignition Delay

As described earlier, the ignition delay in a diesel engine is defined as the time between the start of fuel injection and the start of combustion. In this study, the ignition delay was calculated as the time between when the injection line pressure reached 207 bar and when the change occurred in the slope of the heat release rate at the start of combustion. The heat release calculation was described in Chapter 4.

Table 6.13 and Figure 6.14 show the ignition delay data for the fuels. For the neat methyl esters, the ignition delays were shorter than for the No. 2 diesel fuel. The ignition delay for No. 2 diesel fuel, 20% SME, 20% YGME, SME, and YGME were 6.09°, 6.07°, 6.10°, 5.34°, and 5.46°, respectively. The SME and YGME fuel both had about 0.75° and 0.63° shorter ignition delays than No. 2 diesel fuel, respectively. Monyem [78] also found 0.6° shorter ignition delay when fueling the engine with soybean oil methyl ester compared with No. 2 diesel fuel.

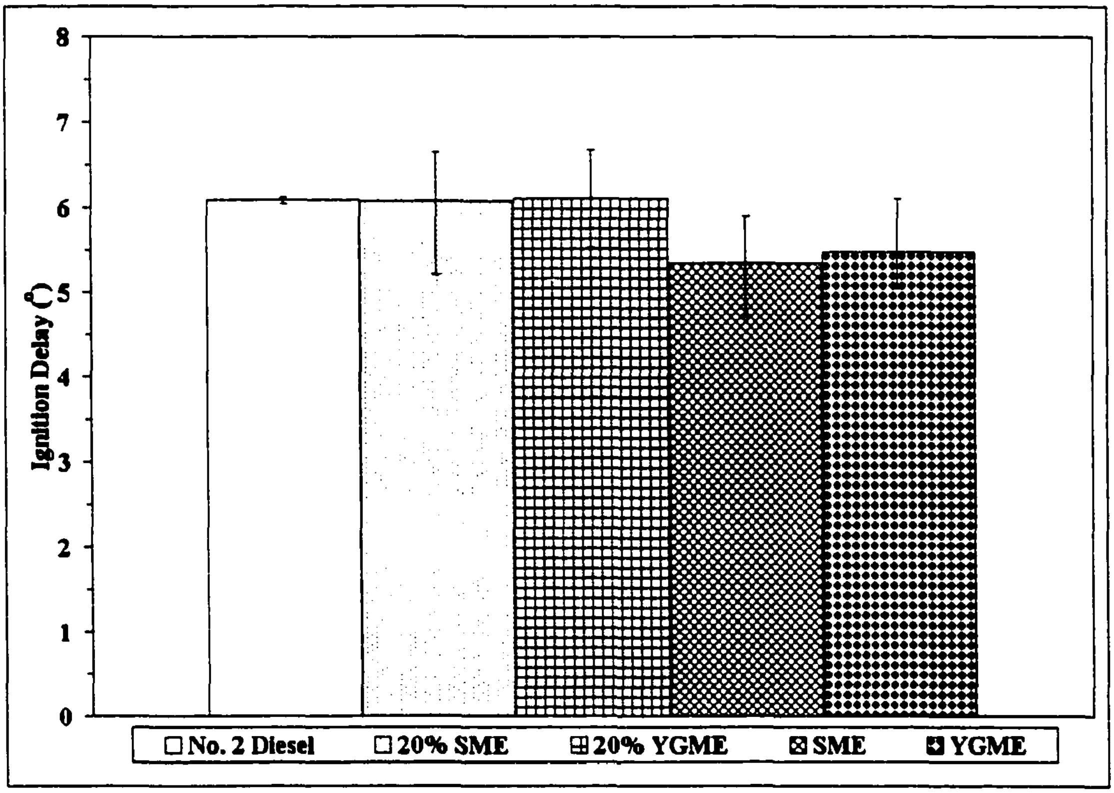


Figure 6.14: Ignition delay of the fuels

The Tukey Grouping test result for the ignition delay is shown in Table 6.16 and the ANOVA table is in Appendix F. The tables show that the ignition delays for the biodiesel fuels were significantly different from the No. 2 diesel fuel. The 20% blends of the biodiesel were not significantly different from the No. 2 diesel fuel. However, there was no statistically significant difference between the two methyl esters or between the two blends.

The physical and chemical properties of the fuels will affect the ignition delay period,

Table 6.16: Tukey Grouping test for variable: Ignition delay

Tukey Grouping	Mean	N	FUEL
A	6.0967	3	20% SME
A	6.0867	3	No. 2 Diesel
A	6.0700	3	20% YGME
B	5.4633	3	SME
B	5.3433	3	YGME

Minimum Significant Difference = 0.5127

and researchers have stressed that chemical properties are much more important than physical properties [91, 107, 108]. The ignition quality of a fuel is usually characterized by its cetane number. Higher cetane number generally means shorter ignition delay. The cetane numbers of the tested fuels were shown in Table 6.2. The cetane numbers for No. 2 diesel fuel, SME, and YGME were 42.6, 51.5, and 62.6, respectively. The cetane number of the esters from soybean oil and yellow grease were 21% and 47% higher than the cetane number of the diesel fuel. The difference between the SME and YGME was expected because both Freedman and Bagby [109] and Van Gerpen [110] have pointed out that saturated esters have higher cetane numbers than unsaturated esters and the YGME is more saturated than the SME.

6.4. Observed Trends in Engine Emissions and Combustion Characteristics

In this section, the effect of the fuels on the pressures in the injection line and the effect of the combustion characteristics on exhaust emissions will be discussed. The discussion of the exhaust emissions will start with the effect of the ignition delay on the unburned HC and CO emissions. Then, the effect of the start of fuel injection on the smoke number and the effect of the start of fuel injection and the start of combustion on the NO_x emissions will be presented.

6.4.1. Effect of the Fuels on the Pressures in the Injection Line

The physical properties of the fuel, such as compressibility and the speed of sound, will affect the pressure in the injection line. The fuels tested in this study have different physical properties and some of the properties for the fuels were shown in Table 6.2. Table 6.17 and Figure 6.15 show how the injection line pressures changed for the fuels used in this study. The timings for the start of injection pressure rise were determined to be the point when the injection pressure first starts to rise in the line. The difference between the start of injection pressure rise and the start of injection was identified as the pressure rise time as shown in the Table 6.17. As seen in the table, No. 2 diesel fuel has the latest start of injection pressure rise, and the methyl esters have earlier starts of injection pressure rise. The timings for the start of injection pressure rise for No. 2 diesel fuel, 20% SME, 20%YGME, SME, and YGME were 17.58°, 18.58°, 18.75°, 20.33°, and 21.33° BTDC, respectively. The SME and YGME fuels both had about 2.75° and 3.75° earlier start of injection pressure rise than No. 2 diesel fuel, respectively. Therefore, the start of injection for the fuels shows a similar trend with the start of the injection pressure rise. However, the pressure rise times, shown in Table 6.17 and Figure 6.16, were almost the same for all the fuels.

Table 6.17: Injection line pressure behavior of the fuels

Fuel	*Start of Injection Pressure Rise (°BTDC)*	*Start of Injection (°BTDC)*	*Pressure Rise Time (°)*
No. 2 Diesel	17.58	13.50	4.08
20% SME	18.58	14.40	4.18
20% YGME	18.75	14.60	4.15
SME	20.33	16.18	4.15
YGME	21.33	17.05	4.28

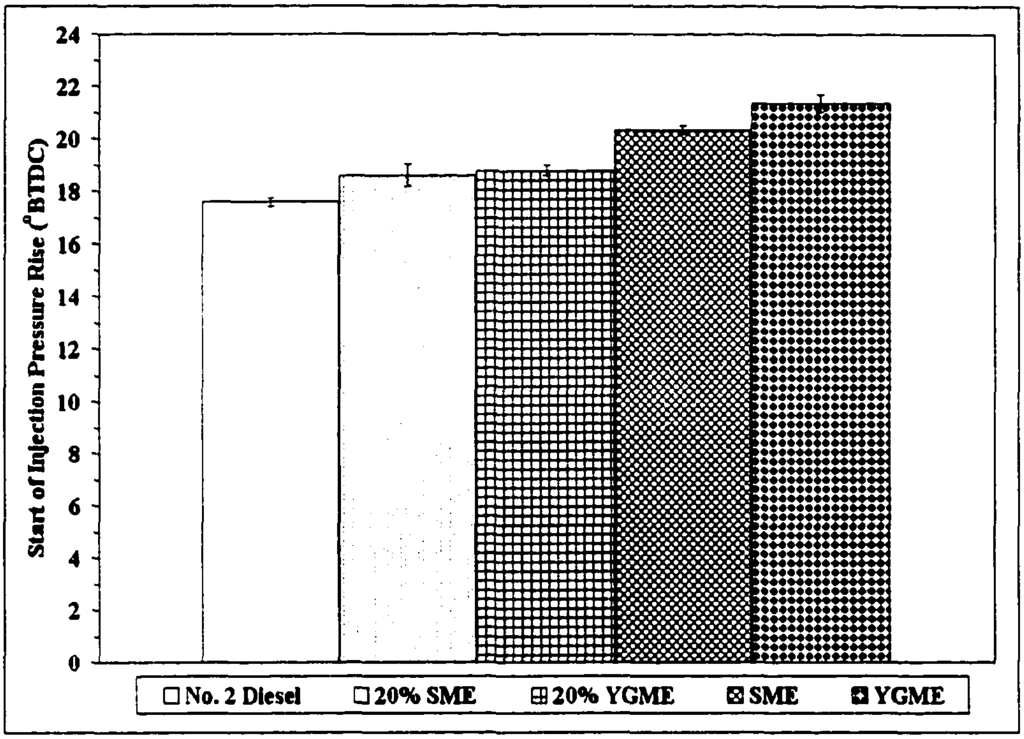


Figure 6.15: Start of injection pressure rise of the fuels

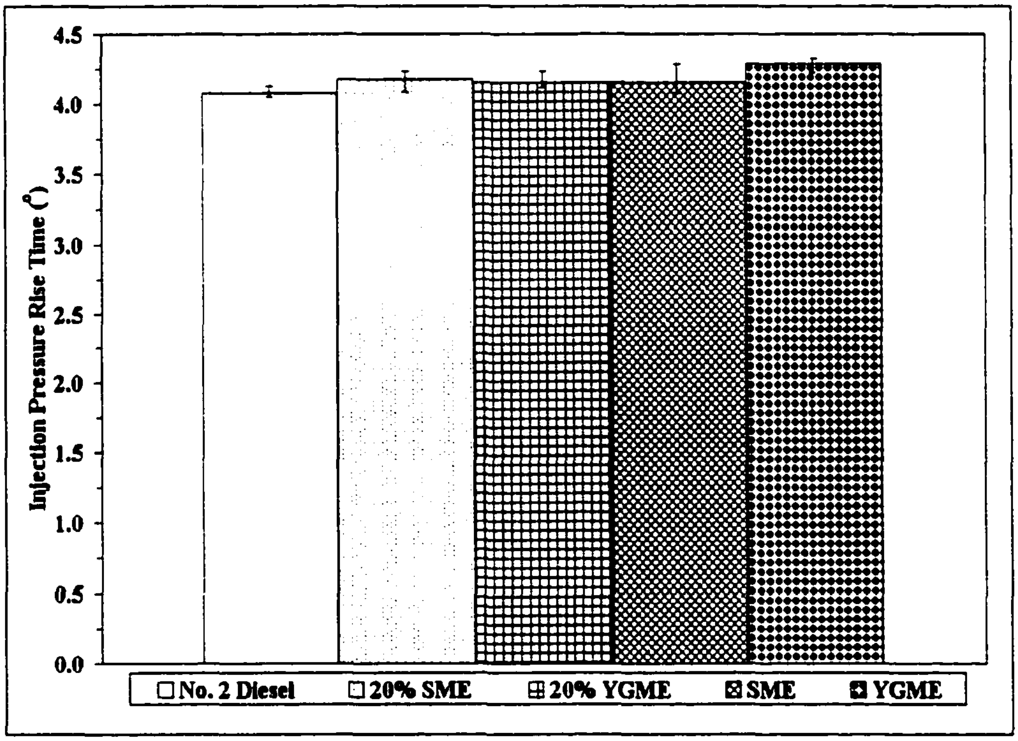


Figure 6.16: Injection pressure rise time of the fuels

6.4.2. Effect of Ignition Delay on Unburned HC and CO Emissions

Hydrocarbons in the exhaust are the consequence of incomplete combustion of the hydrocarbon fuel. Fuel composition can significantly influence the magnitude of the organic exhaust emissions. Fuels containing high proportions of aromatics produce higher concentrations of hydrocarbon in the exhaust [91]. The aromatics content of the fuel also directly affects the cetane number [111]. Another factor that affects unburned hydrocarbons is the ignition delay. Longer ignition delay causes more unburned HC production in the exhaust [112]. Higher cetane number means shorter ignition delay. The No. 2 diesel fuel used in this study contained 35.7% aromatics, and both methyl esters contained no aromatics. Monyem [78] showed there was a linear relationship between the ignition delay and the unburned HC in the exhaust. Figure 6.17 shows the correlation between the unburned HC and ignition delay. While there are too few data points shown in Figure 6.17 to accurately identify the type of relationship between HC and ignition delay, the general trend is consistent with that identified by Monyem [78]. The unburned HC amount decreased as the ignition delay become shorter. Both neat biodiesels, which had shorter ignition delays than the No. 2 diesel fuel, had less HC in the exhaust. The two biodiesel blends, which had identical ignition delays to the No. 2 diesel fuel, had similar amounts of HC in the exhaust as the No. 2 diesel fuel.

The CO emissions also increase with the aromatics content of the fuel since aromatics exhibit slower combustion and, in some cases, do not allow the reaction to go to completion [108]. With shorter ignition delay, the biodiesel fuels have slightly more time to complete the reaction to proceed from CO to CO_2. Figure 6.18 shows the correlation between CO and ignition delay. The CO amount in the exhaust decreased as ignition delay becomes shorter.

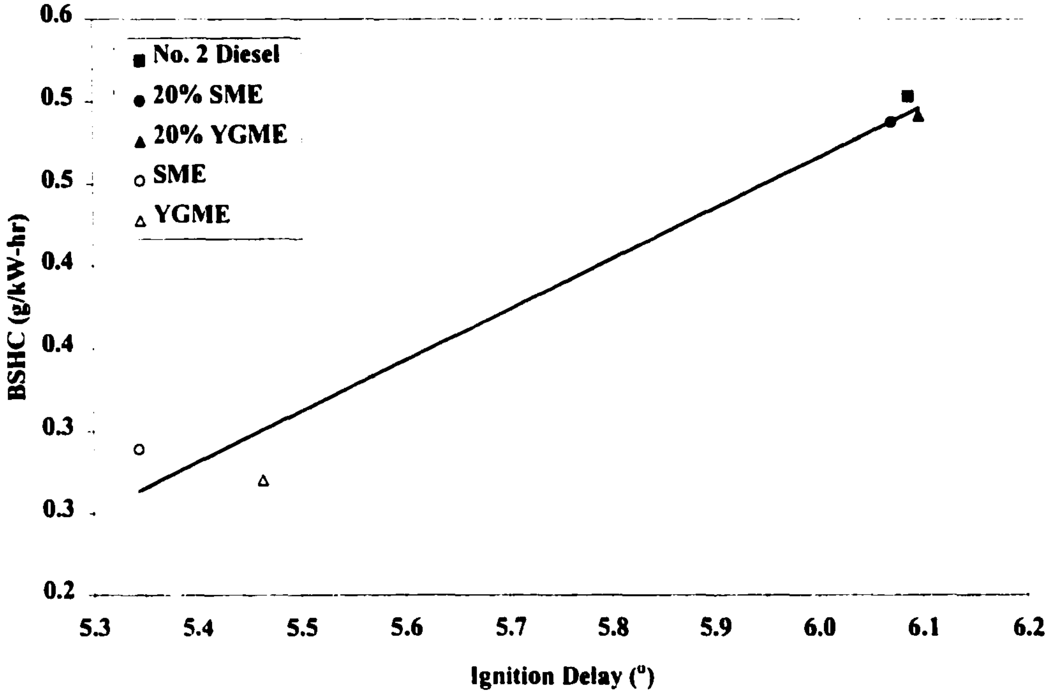


Figure 6.17: Effect of ignition delay on BSHC

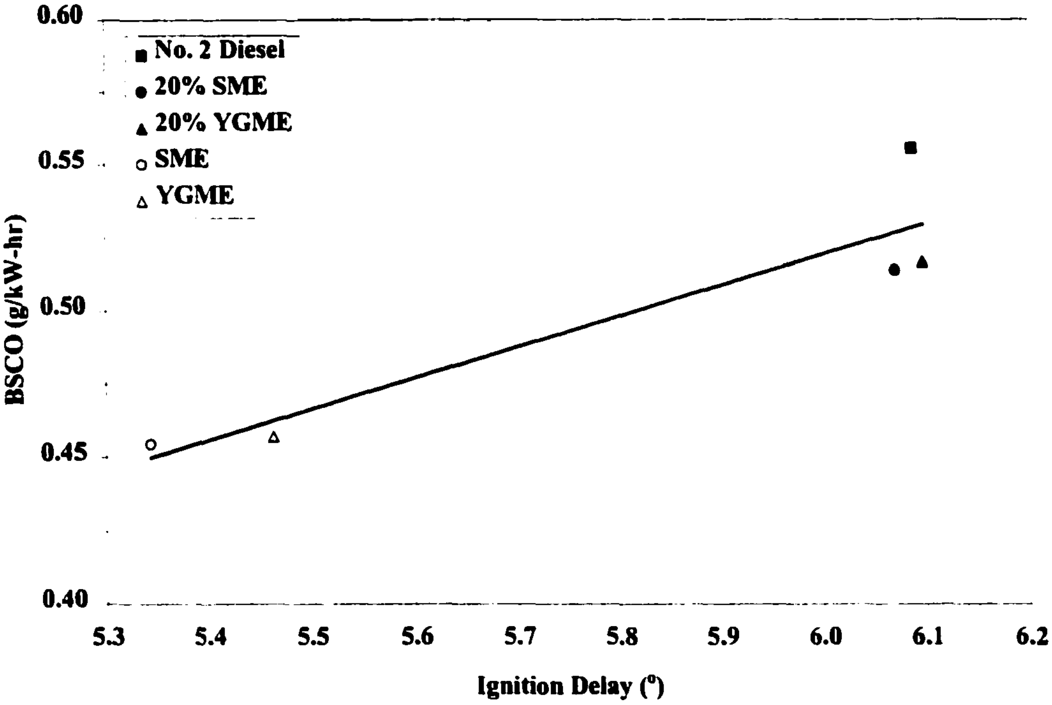


Figure 6.18: Effect of ignition delay on BSCO

Monyem [78] found a linear relationship between ignition delay and CO emission and the data presented here are consistent with that observation.

6.4.3. Effect of Start of Fuel Injection on Smoke Number

Soot particles are primarily produced from the carbon contained in the fuel and depend on the type of fuel, the number of carbons in the molecule, and the C/H ratio of the fuel. Another reason for the soot emissions in the exhaust is the balance of soot formation and oxidation reactions. It has been found that the carbon/oxygen (C/O) ratio is an important factor in the soot oxidation [111]. The C/H ratios of the tested fuels were shown in Table 6.2. The C/H ratios for No. 2 diesel fuel, SME, and YGME were 6.82, 6.53, and 6.24, respectively. The SME and YGME fuel both had 0.29% and 0.58% lower C/H ratio than No. 2 diesel fuel, respectively. However, both biodiesels contained around 11% oxygen.

Figure 6.19 shows the relationship between the start of injection and the smoke number. Both biodiesels had earlier timings for the start of fuel injection than for No. 2 diesel fuel. Both biodiesels showed lower smoke numbers than No. 2 diesel fuel which had the highest smoke number among the fuels. The intermediate points seen in the figure are the blends. Yahya [103] found a significant reduction in smoke number of from 81% to 85% compared to No. 2 diesel fuel when he fueled the engine with soybean oil-based biodiesel. Monyem [78] also studied the effect of the injection timing on the smoke number and found similar results.

6.4.4. Effect of Start of Fuel Injection and the Start of Combustion on NO_x Emissions

Nitric oxide (NO) and nitrogen dioxide (NO_2) are usually grouped together as NO_x. The formation of NO_x depends very strongly on the temperature. It is also highly dependent

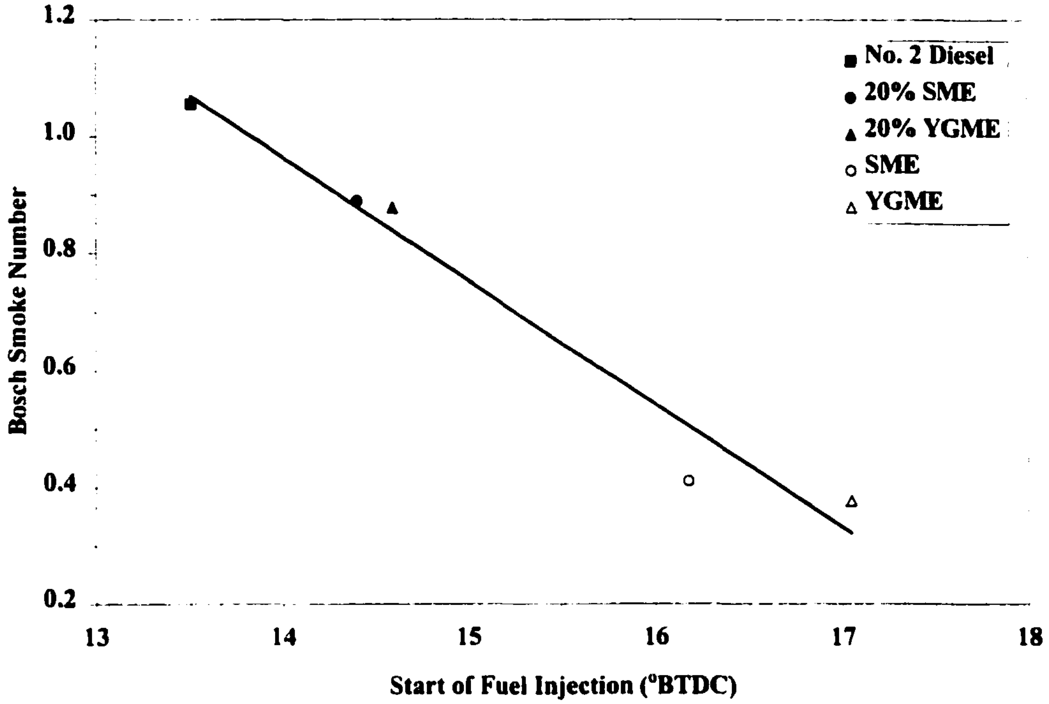


Figure 6.19: Effect of start of fuel injection on smoke number

on oxygen concentration. Accordingly, high temperature and high oxygen concentration increase the quantities of NO_x produced in the exhaust. The main factor that affects oxygen concentration is the overall fuel/air ratio. NO_x emissions are roughly proportional to the quantity of fuel in diesel combustion. The start of injection also effects the NO_x formation. If fuel injection is delayed, combustion starts later and the temperature peak will be lower [111].

The relationship between the start of fuel injection and the NO_x emissions is shown in Figure 6.20. Both biodiesels had earlier timings for the start of fuel injection than for No. 2 diesel fuel. Other researchers [3, 16, 67, 102] have observed that NO_x emissions appear to be linearly related to the timing of the start of fuel injection.

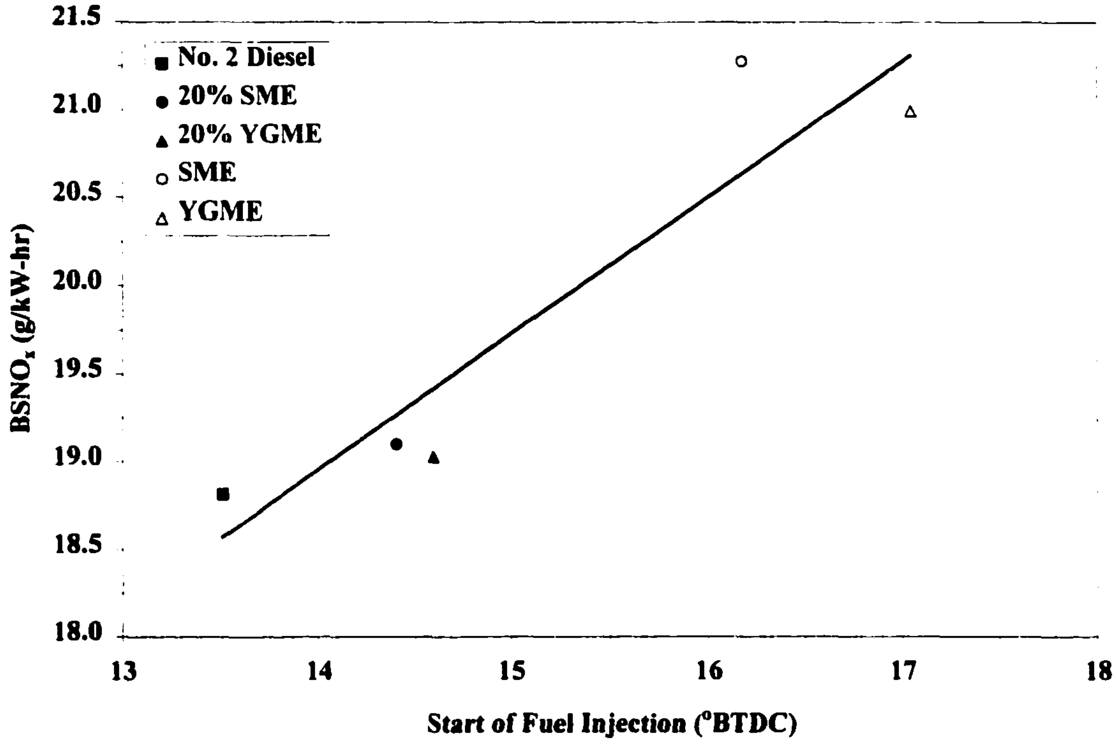


Figure 6.20: Effect of start of fuel injection on BSNO$_x$

As mentioned earlier, the delay in the start of fuel injection results in later combustion. The relationship between the start of combustion and the NO$_x$ emissions is shown in Figure 6.21. The neat biodiesels had earlier timings for the start of combustion than for No. 2 diesel fuel. A similar result was obtained by Monyem [78]. Another reason for the advanced start of combustion for the neat biodiesels was their higher cetane numbers. The ignition delay period for the higher cetane number fuel is shorter than for the lower cetane number fuel. So the higher cetane number fuel will ignite earlier than the lower cetane number fuel.

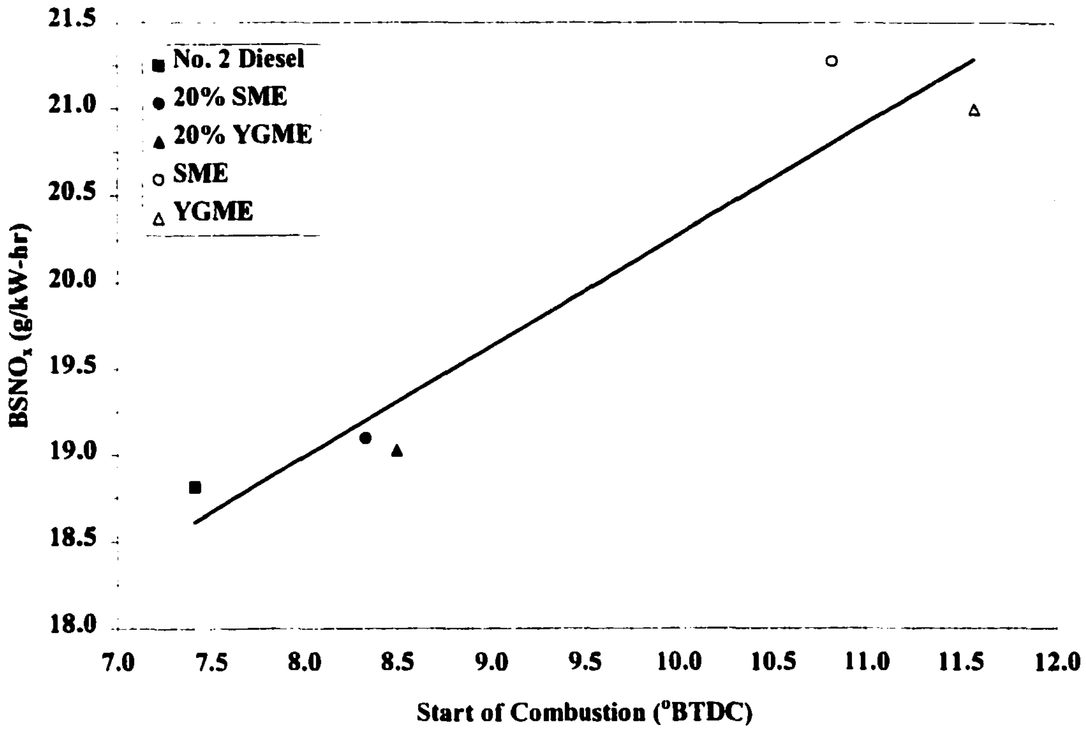


Figure 6.21: Effect of start of combustion on BSNO$_x$

7. CONCLUSIONS AND RECOMMENDATIONS

The objective of this study was to investigate the use of low-cost, high free fatty acid feedstocks to produce commercially viable biodiesel. To accomplish this objective the following tasks were identified.

- Develop a technique to convert high free fatty acid feedstocks to fuel quality biodiesel.
- Implement the biodiesel production technique in a pilot plant.
- Compare the performance and emissions of a diesel engine fueled with biodiesel from high free fatty acid feedstocks with biodiesel from soybean oil and with petroleum-based diesel fuel.

The following sections describe the main conclusions that were derived from accomplishing these three tasks. The last section makes some recommendations for future work.

7.1. Process Development

In the early part of this project, the experiments showed that feedstocks with high free fatty acids could not be transesterified with the alkaline catalysts which 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. It was determined that acid catalysts could be used for transesterification and do not have these disadvantages. Therefore, the effect of the molar ratio of alcohol, reaction temperature, catalyst amount, reaction time, water, and FFA level on the preparation of methyl ester from soybean oil was studied in an acid-catalyzed transesterification reaction with sulfuric acid catalyst.

After the acid-catalyzed reaction with soybean oil was understood, a synthetic high FFA feedstock was prepared by adding a pure FFA to soybean oil and tests were conducted to investigate the preparation of methyl ester from the material with high FFA. In this part of the project, the effect of variables such as methanol molar ratio, acid catalyst amount, and reaction time on the reduction of FFA level were studied. 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. It was concluded that the high FFA feedstocks were most efficiently transesterified by a combination of acid-catalyzed pretreatment followed by an alkaline-catalyzed main reaction.

In the final step of the process development, actual samples of high FFA feedstocks such as yellow and brown grease were processed and compared to the simulated high FFA feedstock study. In this part of the study, the effect of different alkaline catalysts and their amounts on the main transesterification reaction, the residual soap, and the residual catalyst were analyzed. The effect of the solubility of the alcohol, the number of steps in the acid-catalyzed pretreatment reaction, and the alkaline catalyst type and amount on the yield were also discussed. The following specific conclusions are based on the process development portion of this project.

1. Acid-catalyzed transesterification is much slower than alkali-catalyzed transesterification. The ester conversion efficiency is strongly affected by the molar ratio of alcohol to oil. In acid-catalyzed esterification, a higher molar ratio is required than for alkali-catalyzed. The completeness of ester formation increased with increasing acid catalyst amount.
2. Alcohols with high boiling temperature increase ester conversion. The higher reaction

temperatures allowed by longer chain alcohols apparently dominate any tendency toward reduced reaction rates for these alcohols.

3. The ester conversion is strongly inhibited by the presence of water in the oil. If the water concentration is greater than 0.5%, the ester conversion rate may drop below 92%. The amount of free fatty acids in the feedstock oil or fat can also have a significant effect on the transesterification reaction. The water formed by the esterification of the free fatty acids inhibits further reaction. Free fatty acid levels above 5% can lower the ester conversion rate below 90%.
4. 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.
5. In acid-catalyzed esterification, a higher molar ratio of alcohol to oil is required to decrease the acid value of the feedstock. If a lower molar ratio is used, the FFA level of the feedstock requires much more time to reach acceptable levels.
6. Increasing the acid catalyst amount is very effective in decreasing the acid value of the mixture. In the first step, at a 10:1 molar ratio for 30 minutes of reaction time, the acid value of the mixture (41.33 mg KOH/g as palmitic acid) was reduced to 1.37 mg KOH/g and 7.15 mg KOH/g for 15% and 3% acid catalyst, respectively.
7. Ethanol, which has a higher boiling temperature than methanol, decreased the FFA level of the synthetic mixture faster than methanol. The higher reaction temperatures may be the reason for this difference.

8. With KOH as the alkaline catalyst, it was found that 1 mg KOH/g (0.5% FFA) was a better target for acid value reduction. After decreasing the acid value of the feedstock to less than 0.5% FFA level, the KOH-catalyzed transesterification gave good ester conversion.
9. The two-step acid catalysis pretreatment process was successful in decreasing the acid value of yellow grease to less than 1 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.
10. After pretreating yellow grease to decrease its acid value to less than 1 mg KOH/g, the alkaline catalyst transesterification gave good ester conversion. The alkaline catalyst type is an important factor and the best yield, 82.2%, was obtained with 0.35% metallic sodium.
11. The pretreatment reaction can be accomplished in a 1-step process without separation and at a higher molar ratio. But for this case, more excess alkaline catalyst is required to neutralize the acid level of the mixture in the transesterification reaction. This type of process reduced the ester yield.
12. It was observed that the alkaline catalyst amount and type effect the transesterification reaction completeness and yield. $NaOCH_3$ is much stronger than KOH. The best result was obtained with 0.21% $NaOCH_3$ with a 2-step pretreatment and the yield, total glycerin, and specific gravity were 75.12%, 0.1772%, and 0.8748, respectively.
13. In the glycerin separation and biodiesel washing process, it was observed that most of the soap and catalyst were removed with the glycerin phase for soybean oil. For yellow and brown grease, the glycerin did not separate but could be removed by water washing.

7.2. Pilot Plant Development

Another task of this project was to implement the biodiesel production technique in a pilot plant. Therefore, a pilot plant was built in the BECON Facility in Nevada, Iowa. A large number of tests were run to optimize the pilot plant for biodiesel production.

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 3 case studies that were presented for producing biodiesel from soybean oil, yellow grease with 9% FFA, and brown grease with 40% FFA.

1. The results showed that the method developed in small-scale biodiesel production was valid for large-scale production if good mixing was maintained. The mixing process is very important in determining the completeness of the transesterification reaction and on the product yield.
2. The two-step acid catalysis process was successful in decreasing the acid values of the yellow grease and brown grease to less than 2 mg KOH/g. However, the brown grease required 10% acid catalyst in the 2-step pretreatment reaction. After decreasing the acid value of the feedstocks, alkaline catalyst transesterification gave good ester conversion and the biodiesels met the total and free glycerin specifications.
3. Glycerin separation takes a longer time following transesterification of pretreated yellow grease and brown grease than for soybean oil. The number of washing cycles is very important and affects the total glycerin amount in the ester produced from pretreated feedstocks with high FFA. When the number of washing cycles was increased from 4 to 6, the total glycerin amount in the ester decreased from 0.29% to 0.23%.

4. The costs to produce biodiesel from soybean oil, yellow grease with 9% FFA, and brown grease with 40% FFA were compared to each other. The average costs for soybean oil-based methyl ester, YGME, and BGME were $1.584, $1.177, and $0.911, respectively. These costs do not include capital costs.

7.3. Engine Performance and Emissions Evaluation

The final task of this study was to compare the performance and emissions of a diesel engine fueled with biodiesel from a high FFA feedstock, with biodiesel from soybean oil and with No. 2 diesel fuel. The following conclusions can be drawn from the experimental results of this part of the study.

1. Both of the methyl esters and their blends gave nearly identical thermal efficiency with No. 2 diesel fuel. The BSFCs for the esters were higher than for diesel fuel. The increases in BSFC were 13.53% and 14.24% for the neat SME and YGME, respectively. The reason for the higher BSFC for the neat esters may be attributed to their lower heating values. The heating values of the methyl esters are about 12% less than for No. 2 diesel fuel.
2. The neat SME and YGME, and their blends, produced lower CO emissions than No. 2 diesel fuel. The reduction in CO emissions was 18.22% for SME and 17.77% for YGME. There was almost no difference between the CO emissions of the neat methyl esters. There was almost no significant difference between the CO_2 emissions of the all fuels used in the engine test. The HC emission levels from neat SME and YGME were lower than for No. 2 diesel fuel. The reduction in HC emissions was 42.50% for SME and 46.27% for YGME. The Bosch Smoke Number (SN) was significantly reduced when the

engine was fueled with the methyl esters and their blends. The reduction in SN was 61.05% for neat SME and 64.21% for neat YGME.

3. The neat methyl esters had higher NO_x emissions than the No. 2 diesel fuel. The increase in NO_x was 13.09% with SME and 11.60% with YGME. However, the NO_x levels of the 20% blends were close to No. 2 diesel fuel.
4. For the neat methyl esters, the start of fuel injection was earlier than for the No. 2 diesel fuel. The SME and YGME fuel both injected about 2.68° and 3.55° earlier than No. 2 diesel fuel, respectively. For the neat methyl esters, the timings for the start of combustion were earlier than for the No. 2 diesel fuel. The start of combustion for No. 2 diesel fuel, 20% SME, 20%YGME, SME, and YGME were 7.42°, 8.33°, 8.50°, 10.83°, and 11.58° BTDC, respectively. The SME and YGME fuel both started to burn about 3.41° and 4.16° earlier than No. 2 diesel fuel, respectively.
5. For the neat methyl esters, the ignition delay periods were slightly shorter than for the No. 2 diesel fuel. The ignition delay for No. 2 diesel fuel, 20% SME, 20% YGME, SME, and YGME were 6.09°, 6.07°, 6.10°, 5.34°, and 5.46°, respectively.

7.4. Recommendations for Future Work

This section makes several suggestions based on this experiment. These suggestions will provide additional information about biodiesel production from high FFA feedstocks and about its effect on engine performance and emissions.

1. The reasons for the differences in the effectiveness of the acid catalyst pretreatment reaction between the synthetic mixture and the yellow and brown grease feedstocks should be investigated.

2. Recovery of glycerin and methanol in biodiesel production should be studied and a recovery unit should be added to the pilot plant to reduce the cost of the biodiesel from high FFAs.
3. To increase the biodiesel yield, the ester and feedstock lost in the methanol-water mixture separation should be recovered during the pretreatment of the feedstock.
4. The effect of different alcohol types on the cold temperature properties of the biodiesel from high FFA feedstocks should be evaluated.
5. Since biodiesel from high FFA feedstocks contains more saturated components than biodiesel from vegetable oil, the oxidation stability of biodiesel produced from feedstocks with high FFA should be investigated as a possible performance advantage.
6. Durability testing for the biodiesel produced from feedstocks with high FFA would provide information about whether the saturated biodiesel has any effect on the engine components.

APPENDIX A:
AOCS OFFICIAL METHOD CA 14-56 FOR TOTAL, FREE AND COMBINED GLYCEROL TEST [95]

Definition: This method determines total, free and combined glycerol in fats and oils. The total glycerol is determined after saponification of the sample, the free glycerol directly on the sample as taken and the combined glycerol by difference.

Scope: Applicable to the determination of total and free glycerol in fats and oils.

Apparatus:

1. Buret, 50 ml, accurately calibrated.
2. Meniscus magnifier suitable to permit reading the buret to 0.01 ml.
3. Flask, 1 liter volumetric with glass stopper.
4. Pipettes, volumetric, 10 ml, 25 ml, 50 ml and 100 ml. The 25-mL and 50 ml must conform to NBS tolerances and accurately calibrated to deliver 25 and 50 ml.
5. Beakers, 400 ml and watch glasses to serve as covers.
6. Variable speed electric stirrer with glass stirrer.
7. Graduated cylinders, 100 ml and 1,000 ml.
8. Erlenmeyer flasks, borosilicate glass, 250 or 300 ml, and air condensers 65 cm long. The flasks and condensers should have 24/40 ground glass joints.

Reagents:

1. Periodic acid ($HI0_4 \cdot 2H_20$), reagent grade, purchased from a chemical supplier (see Notes, Caution).
2. Sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$, reagent grade.
3. Potassium iodide (KI), reagent grade.
4. Glacial acetic acid, reagent grade, 99.5% (see Notes, Caution).

5. Starch solution, prepared as noted in Solution, item 4, tested for sensitivity as follows- Place 2 ml of starch solution in 100 ml of distilled water and add 0.05 ml of 0.1 N iodine solution. The deep blue color produced must be discharged by 0.05 ml of 0.1N sodium thiosulfate.
6. Chloroform ($CHCl_3$), reagent grade (see Notes, Caution and Recommendation). Blank tests with periodic acid with and without chloroform must agree within 0.5 ml. If they do not, a fresh supply of chloroform must be obtained.
7. Potassium dichromate, reagent grade. The potassium dichromate is finely ground and dried to constant weight at 105 to 110 C before using.
8. Hydrochloric acid (HCl), reagent grade, concentrated, sp. gr. 1.19 (see Notes, Caution).
9. Potassium hydroxide (KOH), reagent grade pellets (see Notes, Caution).
10. Ethyl alcohol, 95%. U.S.S.D Formulas 30 or 3A are permitted (see Notes, Caution).

Solutions:

1. Periodic acid solution, dissolve 5.4 g of periodic acid, in 100 ml distilled water and then add 1900 ml of glacial acetic acid and mix-thoroughly. Store the solution in a dark, glass-stoppered bottle or store in the dark in a clear, glass-stoppered bottle.

Note - Only glass-stoppered bottles should be used. Do not use cork or rubber stoppers under any circumstances.

2. Sodium thiosulfate solution 0.1 N, prepared by dissolving 24.8 g of sodium thiosulfate in distilled water and diluting to 1 liter. The solution is standardized as follows - Pipet 25 ml of the standard dichromate solution (Solutions, 5) into a 400 ml beaker. Add 5 ml of concentrated HC I, 10 ml of KI solution (Solutions, 3) and rotate to mix (a magnetic stirrer and stirring bar may be used). Allow to stand for 5 minutes without mixing and

then add 100 ml of distilled water. Titrate with the sodium thiosulfate solution, stirring continuously until the yellow color has almost disappeared. Add 1 to 2 ml of starch solution and continue the titration, adding the thiosulfate solution *slowly*, until the blue color just disappears. The strength of the thiosulfate solution is expressed in terms of normality -

$$\text{Normality of } Na_2S_2O_3 = \frac{2.5}{\text{ml } Na_2S_2O_3 \text{ required}}$$

3. Potassium iodide (KI) solution prepared by dissolving 150 g of KI in distilled water and dilution 1 liter. Protect this solution from the light.
4. Starch indicator solution, prepared by making a homogeneous paste of 10 g of soluble starch in cold distilled water. Add this paste to 1 liter of rapidly boiling distilled water, stir rapidly for a few seconds and cool. Salicylic acid (1.25 g per liter) may be added to preserve the starch. The solution should be stored in a refrigerator (4 to 10C) when not in use. Fresh indicator must be prepared when the end point of the titration fails to be sharp, or if the starch solution fails the sensitivity test (see Reagents, 5).
5. Standard potassium dichromate solution, 0.1 N prepared by dissolving 4.9035 g of finely ground and dried potassium dichromate in distilled water in a 1 liter volumetric flask and making up to volume at 25 C.
6. Alcoholic KOH solution, prepared by dissolving 40 g of KOH in 1 liter of 95% ethyl alcohol. Filter solution before using if it is cloudy.

Procedure for Total Glycerol:

1. Weigh duplicate samples accurately to ± 0.1 mg into an Erlenmeyer flask. The proper sample size is indicated in Table 1.
2. Add the indicated amount of alcoholic KOH (Table 1), connect the air condenser and gently boil for 30 minutes.
3. Add the indicated amount (Table 1) of chloroform (see Notes, Caution), measured from a buret to within ± 0.2 ml to a 1 liter volumetric flask. Then add with a graduate cylinder 25 ml of glacial acetic acid (see Notes, 1).
4. Remove the saponification flask from the hot plate or steam bath, wash down the condenser with a little distilled water, disconnect the condenser and transfer the sample quantitatively to the volumetric flask, washing the flask, using approximately 500 ml of distilled water.
5. Stopper and shake the flask vigorously for 30 to 60 seconds.
6. Add distilled water to the mark, stopper and mix thoroughly by inverting and set aside until the aqueous and chloroform layers separate.
7. Pipet 50 ml of periodic acid reagent into a series of 400 ml beakers, and prepare two blanks by adding 50 ml of distilled water to each.
8. Pipet 50 of the aqueous layer obtained in step 6 above into a 400-mL beaker containing 50 ml of the periodic acid reagent and shake gently to effect thorough mixing. Cover with a watch glass and allow to stand for 30 minutes (see Notes, 1).

Note - If the aqueous solution contains suspended matter, filter before pipetting the sample for the test.

9. Add 20 ml of KI solution, mix by gently shaking and allow to stand 1 minute (but never

more than 5 minutes) before titrating. Do not allow to stand in bright light or direct sunlight.

10. Dilute the sample to approximately 200-mL with distilled water and titrate with the standardized sodium thiosulfate solution. Continue the titration until the brown iodine color has almost disappeared. Add 2 ml of starch indicator solution and continue the titration until the blue iodine-starch complex color just disappears.
11. Read the buret to nearest 0.01-mL.
12. The blank determinations are handled in exactly the same way as the samples, see Procedure, steps 9 and 10.
13. If the titration of the sample (Procedure, step 11) is less than 0.8 of the titration of the blank (Procedure, step 12), then-
    a) Repeat the test using smaller portions (50, 25, 10 and 5 ml in Procedure, step 8, until the titration of the sample is more than 0.8 of the blank, or
    b) If 10 ml (or less) of the sample solution is necessary to bring the titration within the limit noted in Procedure, step 13, (a), repeat the test starting at the beginning (Procedure, step 8) with a smaller sample of 2 g or less.
14. If the titration of the blank (Procedure, 12), minus the titration of the sample is less than 4 ml, then
    a) Repeat the test using 100 ml in step 8 of Procedure. If the portion taken for the test is still too small, repeat the test beginning with step 1 of Procedure, using twice as much sample, or
    b) If doubling the sample size exceeds 10 g, use only 10 g.

Table 1

Total glycerol (%)	*Approximate size sample (g)*	*Weighing accuracy (g)*	*Alcoholic potassium hydroxide (ml)*	*$CHCl_3$ to be added (ml)*
10 to 40	2	± 0.001	50	99 ± 0.2
5 to 20	4	± 0.003	50	96 ± 0.2
2 to 8	10	± 0.01	100	91 ± 0.2

Procedure for Free Glycerol:

1. Weigh approximately 10-g ± 0.01 g of sample into a weighing dish.
2. Melt the sample by warming on a hot plate and wash into a 1-liter volumetric flask with 90 ml of chloroform, measured from a buret to within ± 0.2-mL.
3. Add approximately 500 ml of distilled water, stopper and shake the flask vigorously for 30 to 60 seconds.
4. Add distilled water to the mark, stopper and mix thoroughly by inverting and set aside until the aqueous and chloroform layers separate.
5. Pipet 50 ml of periodic acid reagent into a series of 400 ml beakers, and prepare two blanks by adding 100 ml of distilled water to each.
6. Pipet 100 ml of the aqueous-layer obtained in step 4 above into a 400-mL beaker containing 50 ml of the periodic acid reagent and shake gently to effect thorough mixing. Cover with a watch glass and allow to stand for 30 minutes (see Notes, 1).

Note - If the aqueous solution contains suspended matter, filter before pipetting the sample for the test.

7. Add 20 ml of KI solution, mix by gently shaking and allow to stand 1 minute (but never more than 5 minutes) before titrating. Do not allow to stan4 in bright light or direct sunlight.
8. Dilute the sample to approximately 200-mL with distilled water and titrate with the

standardized sodium thiosulfate solution. Continue the titration until the brown iodine color has *almost* disappeared. Add 2 ml of starch indicator solution and continue the titration until the blue iodine-starch complex color just disappears.

9. Read the buret to nearest 0.01-mL.
10. The blank determinations are handled in exactly the same way as the samples, see Procedure, steps 7 and 8.
11. If the titration of the sample (Procedure, step 9) is less than 0.8 of the titration of the blank (Procedure, step 12), then repeat the test using a smaller sample size.

Calculations:

1. Report the total glycerol to the nearest 0.1%

$$\text{Total glycerol, \%} = \frac{(B - S) \times N \times 2.302}{W}$$

Where; S= titration of sample

B= titration of blank

N= normality of sodium thiosulfate solution

W= weight of sample represented by aliquot (ml) taken for sample analysis in procedure for total glycerol in which,

$$W = \frac{\text{weight of sample}^{(a)} \times \text{ml of sample}^{(b)}}{900}$$

(a) From Procedure, 1
(b) From Procedure, 8

2. Free glycerol, %, is calculated the same as for total glycerol, using the values obtained as directed in Procedure for Free Glycerol.

3. Combined glycerol in fat or oil, % = (total glycerol in fat or oil, %) - (free glycerol in fat or oil, %).

Notes: *Caution*

Periodic acid is an oxidizing agent and dangerous in contact with organic materials. It is a strong irritant. It decomposes at 130 C. Do not use cork or rubber stoppers on storage bottles.

Chloroform is a known carcinogen. It is toxic by inhalation and has anesthetic properties. Avoid contact with the skin. Prolonged inhalation or ingestion can lead to liver and kidney damage and may be fatal. It is nonflammable, but will burn on prolonged exposure to flame or high temperature, forming phosgene gas when heated to decomposition temperatures. Can react -explosively with aluminum, lithium, magnesium, sodium, potassium, disilane, N_2O_4, and a mixture of sodium hydroxide + methanol. The TLV is 10 ppm in air. A fume hood should be used at all times when using chloroform.

Hydrochloric acid is a strong acid and will cause severe burns. Protective clothing should be worn when working with this acid. It is toxic by ingestion and inhalation and a strong irritant-to eyes and skin. The use of a properly operating fume hood is recommended. When diluting the acid, always add the acid to the water, never the reverse.

Acetic acid in the pure state is moderately toxic by ingestion and inhalation. It is a strong irritant to skin and tissue. The TLV in air is 10 ppm.

Potassium hydroxide, like all alkalies, can burn 'skin, eyes, respiratory tract severely. Wear heavy rubber gloves and face shield to protect against concentrated alkali liquids. Use effective fume removal device or gas mask to protect respiratory tract against alkali dusts or vapors. When working with extremely caustic materials like potassium hydroxide, always add pellets to water and not vice versa. Alkalies are extremely exothermic when mixed with water. Take precautions to contain the caustic solution in the event the mixing container breaks from the extreme heat generated.

Ethyl alcohol (ethanol) is flammable. Use a fume hood when heating or evaporating this solvent.

Precision:

Collaborative studies have shown that the following 95% confidence limits may be expected:

	Total and Combined Glycerol at Level of		Free Glycerol at Level of	
	10.0	0.2	0.5	0.05
Duplicate determinations made on the same day by an analyst should not differ more than approximately.	0.10	0.10	0.01	0.01
Single determinations made in two different laboratories should not differ more than approximately	0.30	0.17	0.17	0.03
Averages of duplicate determinations made in two different laboratories should not differ by more than approximately	0.28	0.14	0.17	0.03

Recommendations

Cyclohexane and iso-octane may be considered as replacements for chloroform in this method. These solvents have not been collaboratively studied within the AOCS, but laboratories may want to try *them on an* experimental basis. This recommendation does not represent official approval by the AOCS Uniform Methods Committee.

Numbered Notes

Samples may be allowed to stand 1.5 hours at room temperature before titrating, but never longer. Do not allow samples to stand in bright light or direct sunlight.

APPENDIX B:
AOCS OFFICIAL METHOD CD 3A-63 FOR ACID VALUE TEST [97]

The acid value is the number of milligrams of potassium hydroxide (KOH) necessary to neutralize the free acids in 1 gram of sample. This method is applicable to crude and refined animal, vegetable, and marine fats and oils, and various products derived from them. The necessary apparatus, reagents, test procedure and the calculations for the acid value test are explained below.

Apparatus:

1. Erlenmeyer flasks, 250 ml.
2. Burette, 50 ml.

Reagents:

1. Potassium hydroxide (KOH), 0.1 N and 0.01N in water.
2. Solvent mixture contains of equal parts by volume of isopropyl alcohol and toluene.
3. Phenolphthalein indicator solution, 1.0% in isopropyl alcohol.

Procedure:

1. Add 0.8 ml phenolphthalein indicator solution to 50 ml of solvent mixture (1:1 isopropyl alcohol - toluene) and neutralize with alkali (0.01N KOH) to a faint but permanent pink color. The amount of alkali (0.01N KOH) used to neutralize the solvent mixture is the blank (B).
2. Determine the sample size from Table 1 by comparing the expected acid value. Higher acid value needs less amount of sample and lower acid value needs a large amount of sample.

Table 1: Sample size for the test

Acid Value	*Wt. of Sample (gm)*
0 to 1	20
1 to 4	10
4 to 15	2.5
15 to 75	0.5
75 and over	0.1

3. Weigh the specified amount of sample from Table A.1 into an Erlenmeyer flask.
4. Add 50 ml of solvent mixture (1:1 isopropyl alcohol - toluene). Be sure that the sample is completely dissolved. Warming may be necessary in some cases.
5. Shake the sample vigorously while titrating with standard alkali (0.1N or 0.01N KOH depending upon intensity of acid value in the sample) to the first permanent pink color of the same intensity as that of the neutralized solvent. The color must persist for 30 seconds. The amount of standard alkali used in this step is A, where A is defined below.

Calculation:

$$\text{The acid value, mg KOH/g of sample} = (A-B) * N * 56.1/W$$

Where; A= ml of standard alkali (0.1N or 0.01N KOH) used in the titration

B= ml of standard alkali (0.1N or 0.01N KOH) used in the titrating the blank

N= normality of the standard alkali (0.1 or 0.01N KOH)

W= grams of sample

APPENDIX C:
SOAP AND CATALYST TEST IN ESTER, WASH WATER, AND GLYCERIN

Soap, free fatty acids and catalyst are treated together because they are related compounds. Most biodiesel is produced using an alkaline catalyst such a sodium methoxide, sodium hydroxide, or potassium hydroxide. Any free fatty acids that are present will react with the alkaline catalyst to form soaps. These soaps are then removed during the washing process. The washing process also removes any residual catalyst.

To investigate the amount of residual catalyst and soap formed during the transesterification reaction, an experiment was conducted to determine the effectiveness of water washing. A batch of methyl ester was produced from a food-grade soybean oil using potassium hydroxide as the catalyst. The methyl ester was separated from the mixture of methyl ester, soap and catalyst by washing with distilled water. The steps of the washing process were as follows. [78]

1. Add 100 cc of distilled water to a 500 ml separatory funnel containing approximately 200 cc of raw methyl ester (mixture of methyl ester soap, catalyst, and unreacted methanol) Shake the distilled water and the raw methyl ester mixture.
2. Wait until the soapy water separates from the mixture.
3. Separate the soapy wash water from the mixture and place into a 150 ml flash for later soap and catalyst tests. The soapy water also contains a portion of the unreacted methanol and catalyst.
4. Repeat steps 1-3 seven times and keep all the wash water samples in 150 ml flasks for measurement of soap and catalyst.

The amount of soap and residual catalyst in the methyl ester was determined by adding a sample of the wash water to a larger quantity of ethanol and titrating with 0.01N HCI using a phenolphthalein indicator solution. The amount of residual catalyst was calculated from the formula:

$$\%\text{Catalyst (as potassium hydroxide)} = \frac{Q_1 * 56.1}{1000 * q} * 100$$

where; Q = milliequivalents of 0.01N HCI added
(milliequivalent =ml of HCL * Normality of HCL)

q = sample size in grams

For the soap measurement, 4-5 drops of bromophenol blue indicator solution was added and the titration continued to the yellow end point. The amount of soap was calculated from the formula:

$$\%\,\text{Soap (as sodium oleate)} = \frac{Q_2 * 304.4}{1000 * q} * 100$$

where; Q_2 = milliequivalents of additional 0.01N HCI added.

APPENDIX D:
CALIBRATIONS OF THE PRESSURE TRANSDUCERS

Two pressure transducers were used to measure cylinder pressure and injection pressure during the engine test. These transducers were Kistler models 6061B and 6230M1. The Table D.1 shows the specifications of these pressure transducers.

Table D.1: Specifications of the pressure transducers

Type	*Application*	*Range*	*Linearity*
Kistler Model 6061B	Cylinder Pressure	0-250 Bar	±0.2 (full Scale)
Kistler Model 6230M1	Injection Pressure	0-250 Bar	-

The pressure transducer produces an electrical charge when pressure applied to its diaphragm, and the charge amplifier produces an output voltage in proportion to this charge. Therefore, calibration is necessary to determine the relationship cf pressure input to voltage output for the system. For the model 6230M1, the factory calibration was used. But before installation the model 6061B pressure transducer, it was calibrated using a dead weight tester and a digital voltmeter. The calibration procedure was to load and unload the known weights on the tester plate. The output signal charged by the transducer was amplified by a PCB Model 462A charge amplifier as a voltage. A Pentium II computer with a Lab-View program recorded the voltage. A linear regression analysis was used to fit a straight line for the collected pressure data as shown in Figure D.1.

For this transducer the general equation to calculate the pressure in the cylinder is as follows:

$$P = A + B * V$$

Where; P = cylinder pressure (bar)

V = voltage output from the transducer

A and B = linear regression coefficients

A = 0.0557

B = 10.177

The Kistler Model 6230M1 pressure transducer was installed in the fuel injection line to measure injection pressure. The sensitivity of this transducer was 1.755 pC/bar. The sensitivity of the charge amplifier was 322 pC/Volt. Using these information, the sensitivity of the pressure transducer was calculated 183.476 bar/Volt.

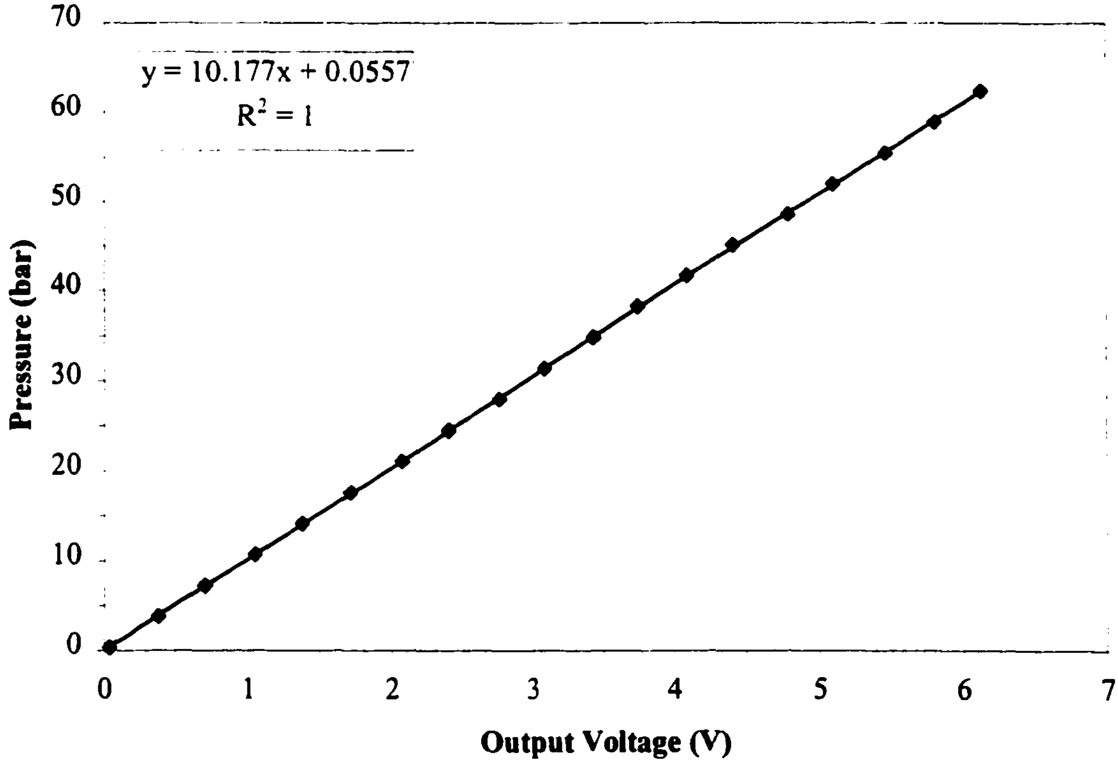


Figure D.1: Calibration of the Kistler model 6061B pressure transducer

APPENDIX E:
CALIBRATION CURVES OF THE EMISSION ANALYZERS

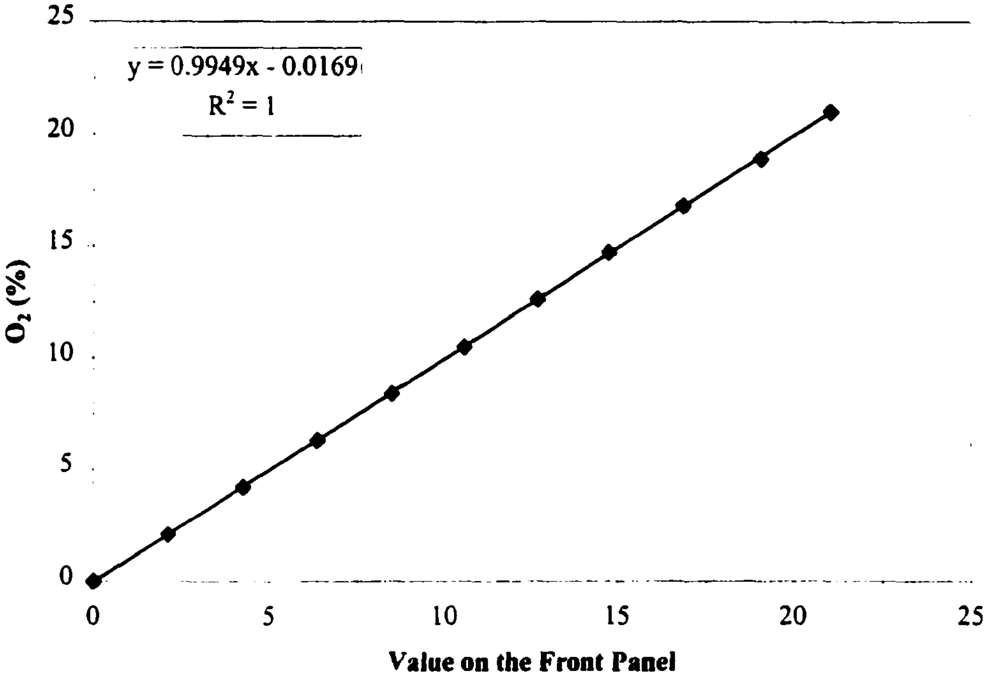


Figure E.1: Calibration curve of O_2 exhaust gas analyzer

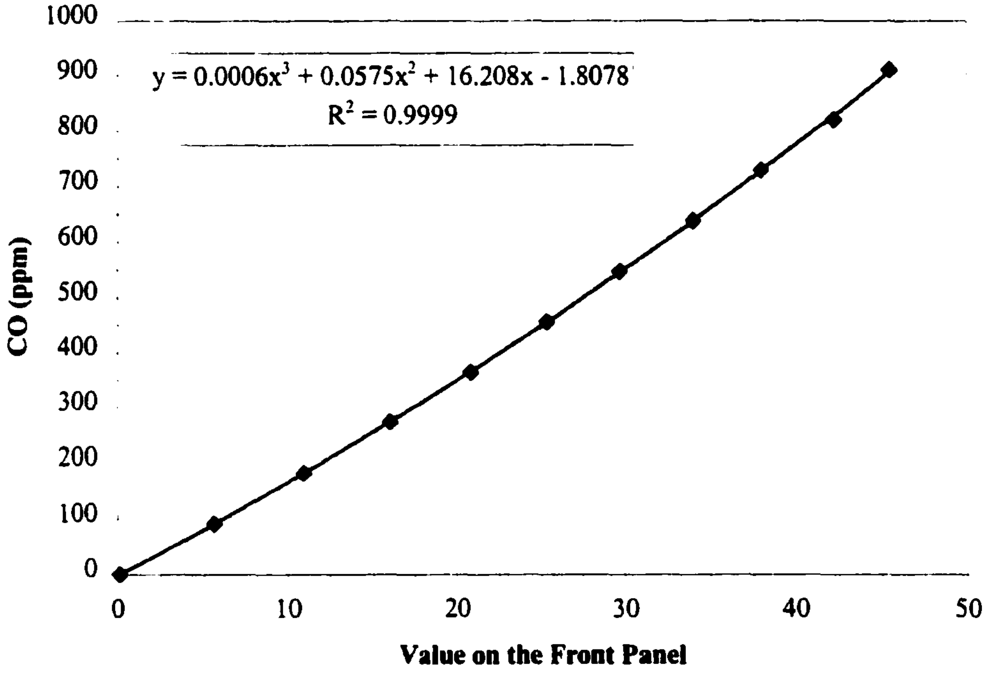


Figure E.2: Calibration curve of CO exhaust gas analyzer

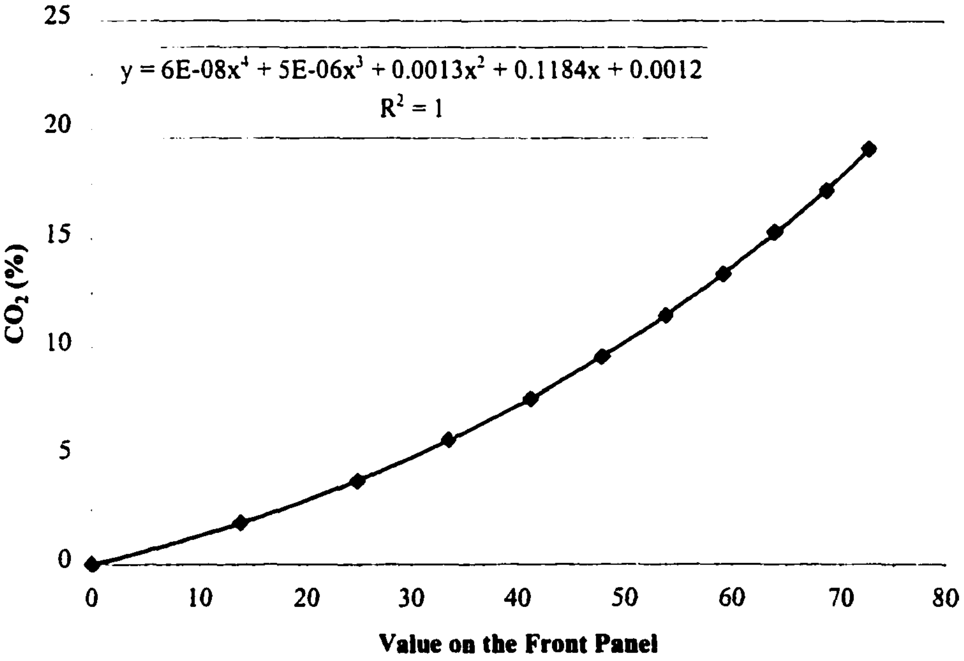


Figure E.3: Calibration curve of CO_2 exhaust gas analyzer

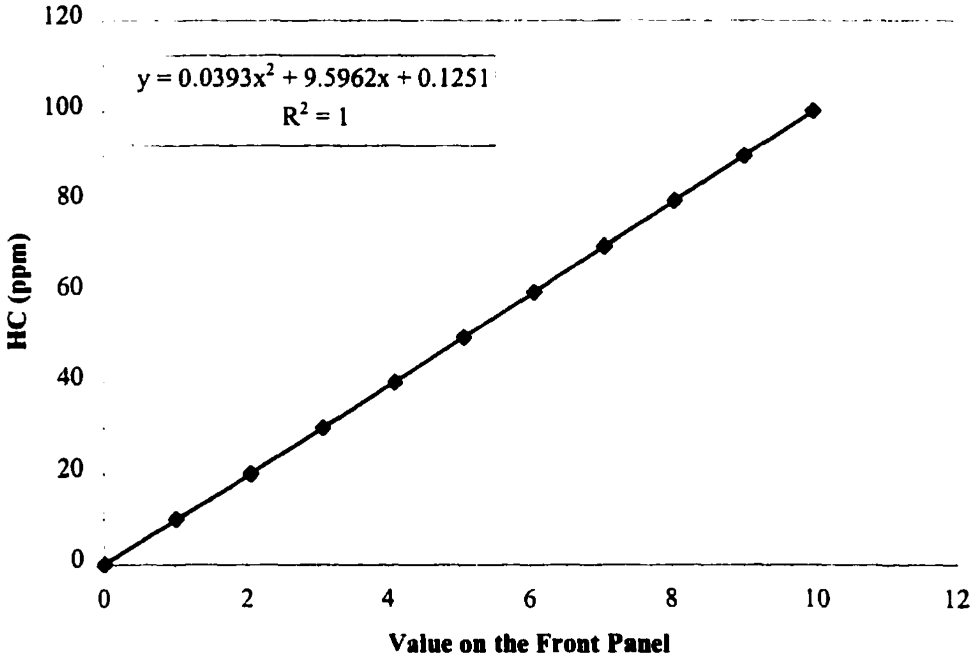


Figure E.4: Calibration curve of HC exhaust gas analyzer

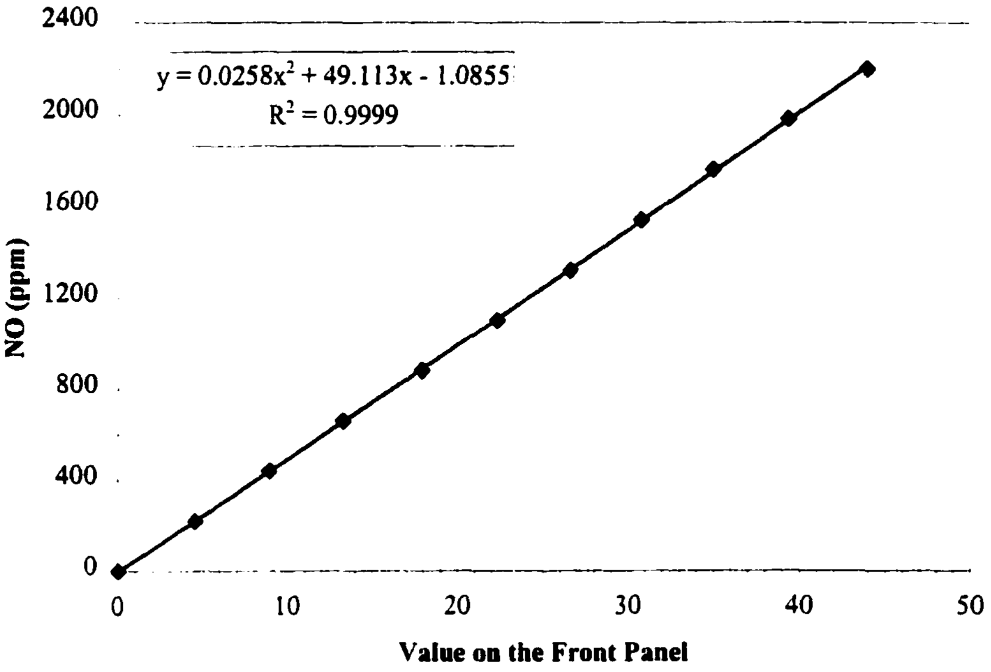


Figure E.5: Calibration curve of NO exhaust gas analyzer

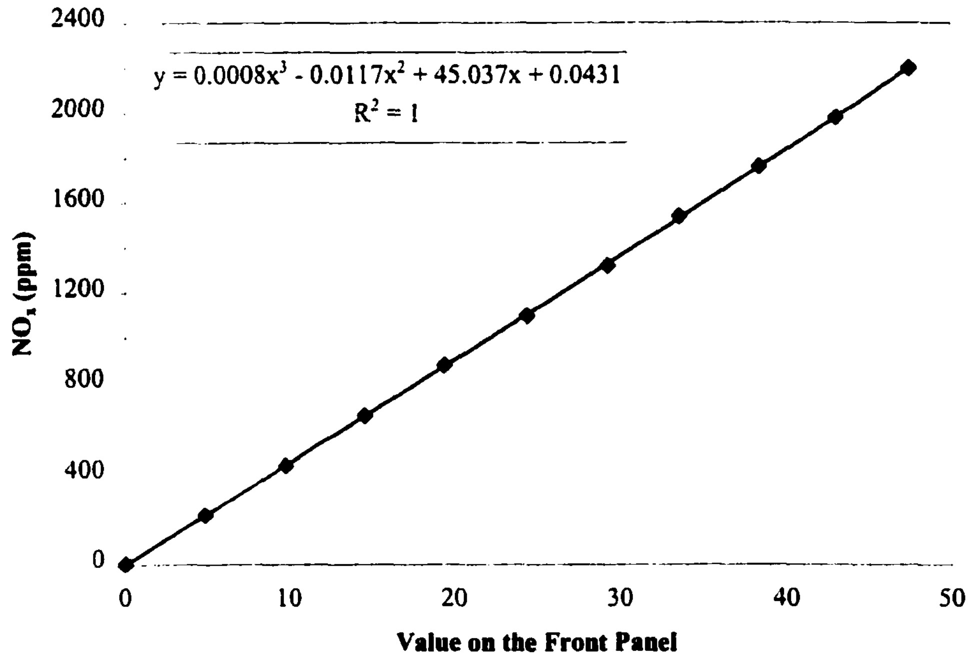


Figure E.6: Calibration curve of NO_x exhaust gas analyzer

APPENDIX F:
ANOVA TABLES

This section contains a sample SAS program written for the statistical analysis and ANOVA tables for engine performance and emissions. In the ANOVA tables, DF represents the degrees of freedom, the F value represents the probability distribution in repeated sampling, and Pr > F represents the probability level. The significance level (Pr > F value) of the fuels on the dependent variable can be identified from the ANOVA tables. For all of the statistical analyses of this study, a 95% confidence interval was used.

A sample SAS program for ANOVA and Tukey's Grouping.

```
FILENAME IN1 'd:\Project4\EngineStatAnalysis\BSCO.dat';

data p;
infile IN1;
input BSCO fuel;

proc format;
value fuelfmt  1='No. 2 Diesel'
               2='20% SME'
               3='20% YGME'
               4='SME'
               5='YGME';
proc anova;
class fuel;
model BSCO = fuel;
format fuel fuelfmt.;
means fuel/TUKEY;
run;
```

Table F.1: Analysis of variance (ANOVA) for BSFC

Dependent Variable: BSFC

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
FUEL	4	2840.868	710.217	659.58	0.0001
Error	10	10.768	1.077		
Corrected Total	14	2851.636			

R-Squared = 0.9962; BSFC Mean = 243.504

Table F.2: Analysis of variance (ANOVA) for brake thermal efficiency

Dependent Variable: Thermal Efficiency

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
FUEL	4	0.135	0.0336	1.31	0.3321
Error	10	0.258	0.0258		
Corrected Total	14	0.392			

R-Squared = 0.3431; Thermal Efficiency Mean = 37.026

Table F.3: Analysis of variance (ANOVA) for BSCO

Dependent Variable: BSCO

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
FUEL	4	0.02276	0.00569	24.95	0.0001
Error	10	0.00228	0.00023		
Corrected Total	14	0.02504			

R-Squared = 0.9089; BSCO Mean = 0.499

Table F.4: Analysis of variance (ANOVA) for $BSCO_2$

Dependent Variable: $BSCO_2$

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
FUEL	4	562.446	140.612	0.90	0.4982
Error	10	1558.076	155.808		
Corrected Total	14	2120.523			

R-Squared = 0.2652; $BSCO_2$ Mean = 807.580

Table F.5: Analysis of variance (ANOVA) for BSHC

Dependent Variable: BSHC

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
FUEL	4	0.1663	0.04157	97.49	0.0001
Error	10	0.0043	0.00043		
Corrected Total	14	0.1706			

R-Squared = 0.9750; BSHC Mean = 0.4083

Table F.6: Analysis of variance (ANOVA) for BSNO$_x$

Dependent Variable: BSNO$_x$

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
FUEL	4	16.989	4.247	87.02	0.0001
Error	10	0.488	0.049		
Corrected Total	14	17.478			

R-Squared = 0.9721; BSNO$_x$ Mean = 19.841

Table F.7: Analysis of variance (ANOVA) for SN

Dependent Variable: SN

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
FUEL	4	1.1359	0.2840	58.96	0.0001
Error	10	0.0482	0.0048		
Corrected Total	14	1.1841			

R-Squared = 0.9593; SN Mean = 0.7223

Table F.8: Analysis of variance (ANOVA) for start of fuel injection

Dependent Variable: Start of Fuel Injection

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
FUEL	4	24.6794	6.1699	37.60	0.0001
Error	10	1.6407	0.1641		
Corrected Total	14	26.3202			

R-Squared = 0.9377; Start of Fuel Injection Mean = 15.1453

Table F.9: Analysis of variance (ANOVA) for start of combustion

Dependent Variable: Start of Combustion

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
FUEL	4	38.0417	9.5104	142.66	0.0001
Error	10	0.6667	0.0667		
Corrected Total	14	38.7083			

R-Square = 0.9828; Start of Combustion Mean = 9.3333

Table F.10: Analysis of variance (ANOVA) for ignition delay

Dependent Variable: Ignition Delay

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
FUEL	4	1.6928	0.4232	1.34	0.0001
Error	10	3.1691	0.3169		
Corrected Total	14	4.8618			

R-Square = 0.9482; Ignition Delay Mean = 5.8120

APPENDIX G:
RAW DATA COLLECTED FOR ENGINE TEST

Table G.1: Raw data collected for engine test in first repetition

Fuel	*#2 Diesel*	*100% SME*	*20% SME*	*100% YGME*	*20% YGME*
Date	8/14/00	8/14/00	8/14/00	8/14/00	8/14/00
Engine Speed (rpm)	1400	1400	1400	1400	1400
Load (%)	100	100	100	100	100
Brake Torque (ft . lbf)	190	190	190	190	190
Patm (mmHg)	737.4	737.4	737.4	737.4	737.4
Ambient Air Temp. (°C)	21	21	21	21	21
Relative Humidity	55	55	55	55	55
Pressure Diff. of LFE (in H_2O)	2.4	2.4	2.4	2.4	2.4
Oil Pressure (psi)	48	47	47.5	47.5	48
Boost Pressure (psi)	2.8	2.8	2.8	2.7	2.8
Exhaust Pressure (psi)	3.1	3	3	3	3
Smoke Number (Bosch)	1.13	0.40	0.97	0.40	0.90
Coolant Count/10 sec.	134.2	136.2	134.1	138.3	124.3
Fuel Consumption (g/min)	144.85	162.55	148.32	163.58	147.87
BSFC (g/kW-hr)	230.09	258.21	235.60	259.84	234.89
Temperature (° F)					
1. Inlet Air Temp.	73	74	74	74	73
2. Inlet Manifold Temp.	118	124	123	124	122
3. Fuel Temp.	104	104	104	104	104
4 Cooling Water Inlet Temp.	154	156	157	156	157
5. Cooling Water Outlet Temp.	172	174	174	174	174
6. Exhaust Manifold Temp.	798	806	809	798	806
7. Exhaust Temp. Shielded	821	808	819	800	814
8. Exhaust Temp. Unshield	804	794	802	787	803
9. Oil Temp.	208	209	209	210	208
10. Building Cooling Water Inlet	66	66	66	66	66
11. Building Cooling Water Outlet	79	79	79	79	79
Emissions:					
O_2 (g/kW-hr)	566.044	557.978	558.643	553.231	561.461
CO (g/kW-hr)	0.563	0.464	0.518	0.482	0.518
CO_2 (g/kW-hr)	777.839	809.608	808.822	803.734	790.740
HC (g/kW-hr)	0.543	0.317	0.477	0.276	0.487
NO (g/kW-hr)	17.459	19.144	18.472	18.982	18.528
NO_x (g/kW-hr)	18.334	21.468	19.050	20.797	19.010
File Names:					
Cylinder Pressure	cyld21.dat	cyls1001.dat	cyls201.dat	cyly1001.dat	cyly201.dat
Injection Pressure	injd21.dat	injs1001.dat	injs201.dat	injy1001.dat	injy201.dat

Table G.2: Raw data collected for engine test in second repetition

Fuel	*#2 Diesel*	*100% SME*	*20% SME*	*100% YGME*	*20% YGME*
Date	8/15/00	8/15/00	8/15/00	8/15/00	8/15/00
Engine Speed (rpm)	1400	1400	1400	1400	1400
Load (%)	100	100	100	100	100
Brake Torque (ft . lbf)	190	190	190	190	190
Patm (mmHg)	741.8	741.8	741.8	741.8	741.8
Ambient Air Temp. (°C)	20	20	20	20	20
Relative Humidity	55	55	55	55	55
Pressure Diff. of LFE (in H_2O)	2.4	2.4	2.4	2.4	2.4
Oil Pressure (psi)	48	47.5	48	47.5	48
Boost Pressure (psi)	2.8	2.7	2.7	2.7	2.7
Exhaust Pressure (psi)	3.1	3.1	3.1	3.1	3.1
Smoke Number (Bosch)	1.23	0.40	0.87	0.33	0.87
Coolant Count/10 sec.	132.6	137.5	131.9	140.1	126.1
Fuel Consumption (g/min)	143.15	163.42	147.18	164.38	147.19
BSFC (g/kW-hr)	227.39	259.59	233.79	261.11	233.81
Temperature (°F)					
1. Inlet Air Temp.	73	73	73	73	73
2. Inlet Manifold Temp.	117	121	119	121	119
3. Fuel Temp.	104	104	104	104	104
4 Cooling Water Inlet Temp.	156	157	155	158	155
5. Cooling Water Outlet Temp.	174	174	174	174	174
6. Exhaust Manifold Temp.	806	804	800	789	807
7. Exhaust Temp. Shielded	819	805	810	796	812
8. Exhaust Temp. Unshield	803	790	795	783	800
9. Oil Temp.	209	210	209	210	208
10. Building Cooling Water Inlet	67	67	68	67	68
11. Building Cooling Water Outlet	80	80	80	80	80
Emissions:					
O_2 (g/kW-hr)	548.255	572.432	569.950	560.907	565.499
CO (g/kW-hr)	0.548	0.449	0.530	0.440	0.530
CO_2 (g/kW-hr)	823.426	819.881	800.953	819.019	808.339
HC (g/kW-hr)	0.476	0.270	0.497	0.278	0.498
NO (g/kW-hr)	18.334	19.293	18.612	19.423	18.225
NO_x (g/kW-hr)	18.984	21.248	19.144	21.140	19.010
File Names:					
Cylinder Pressure	cyld22.dat	cyls1002.dat	cyls202.dat	cyly1002.dat	cyly202.dat
Injection Pressure	injd22.dat	injs1002.dat	injs202.dat	injy1002.dat	injy202.dat

Table G.3: Raw data collected for engine test in third repetition

Fuel	*#2 Diesel*	*100% SME*	*20% SME*	*100% YGME*	*20% YGME*
Date	8/15/00	8/15/00	8/15/00	8/15/00	8/15/00
Engine Speed (rpm)	1400	1400	1400	1400	1400
Load (%)	100	100	100	100	100
Brake Torque (ft . lbf)	190	190	190	190	190
Patm (mmHg)	741.8	741.8	741.8	741.8	741.8
Ambient Air Temp. (°C)	20	20	20	20	20
Relative Humidity	55	55	55	55	55
Pressure Diff. of LFE (in H_2O)	2.4	2.4	2.4	2.4	2.4
Oil Pressure (psi)	48	48	48	48	48
Boost Pressure (psi)	2.7	2.7	2.7	2.7	2.7
Exhaust Pressure (psi)	3.1	3.1	3.1	3.1	3.1
Smoke Number (Bosch)	1.13	0.37	0.87	0.33	0.80
Coolant Count/10 sec.	135.2	135.8	132.8	141.6	122.7
Fuel Consumption (g/min)	143.39	163.79	147.48	164.85	147.41
BSFC (g/kW-hr)	227.77	260.18	234.27	261.86	234.16
Temperature (° F)					
1. Inlet Air Temp.	73	74	73	74	74
2. Inlet Manifold Temp.	118	124	121	123	121
3. Fuel Temp.	104	104	104	104	104
4 Cooling Water Inlet Temp.	157	157	157	156	156
5. Cooling Water Outlet Temp.	174	175	175	175	174
6. Exhaust Manifold Temp.	803	803	805	790	809
7. Exhaust Temp. Shielded	820	813	815	799	815
8. Exhaust Temp. Unshield	804	790	800	786	801
9. Oil Temp.	210	211	210	211	210
10. Building Cooling Water Inlet	69	69	68	69	69
11. Building Cooling Water Outlet	81	80	80	81	80
Emissions:					
O_2 (g/kW-hr)	560.882	566.456	573.530	562.225	571.136
CO (g/kW-hr)	0.557	0.449	0.494	0.449	0.503
CO_2 (g/kW-hr)	807.804	822.615	798.319	814.008	808.591
HC (g/kW-hr)	0.490	0.280	0.489	0.257	0.489
NO (g/kW-hr)	18.678	19.690	18.512	19.722	18.328
NO_x (g/kW-hr)	19.121	21.110	19.095	21.049	19.062
File Names:					
Cylinder Pressure	cyld23.dat	cyls1003.dat	cyls203.dat	cyly1003.dat	cyly203.dat
Injection Pressure	injd23.dat	injs1003.dat	injs203.dat	injy1003.dat	injy203.dat

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