The Optimization of the Esterification Reaction in Biodiesel Production from Trap Grease

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Abstract *In this experimental study, biodiesel production from waste oils (trap grease), which were obtained from an oil separator, was carried out by using sulfuric acid as the catalyst and esterification process. The main variables involved in the esterification process, including methanol/waste cooking oils ratio, amount of acid catalyst, reaction time, and reaction temperature, were analyzed. Because the waste cooking oils contain high free fatty acid above 65%, the esterification process has been preferred. Methanol was used as alcohol in this process because of its low cost, and sulfuric acid was preferred as the catalyst because it gives very high yields in alkyl esters. Experiments have been performed to determine optimum conditions for this esterification process in different molar ratios, catalyst amounts, reaction times, and reaction temperatures. The optimum experimental conditions, which were obtained from the esterification process, were methanol/waste cooking oils ratio 9/1, with 9 wt% sulfuric acid catalyst, reaction time 120 min, and reaction temperature 60°C. The yield of biodiesel was 93.98% at optimum esterification process. Biodiesel and its blends with diesel were characterized for their physical properties referring to a substitute for diesel fuel. The results show that blends with a percentage of the biodiesel below 40 vol% had their physical properties within EN590 standard, which indicated that these could be used in engines without a major modification.*

Keywords biodiesel, esterification, oil separator, trap grease, waste oils

1. Introduction

In its most general sense, because of its similarity to diesel, biodiesel is defined as an alternative fuel for diesel, which is derived from renewable biomass. Biodiesel can be used as a blending component or a direct replacement for diesel fuel in internal combustion engines (Demirbaş, 2009). In contrast to petrodiesel, the advantages of biodiesel are lower emission of CO due to a better combustion, a better lubricating effect on engines, non-sulfur emission, non-flammable, non-explosive with a flash point of 423 K for biodiesel as compared to 337 K for petrodiesel, portability, ready availability, renewability, higher combustion efficiency, lower sulfur, higher cetane number, higher biodegradability, and non-aromatic content (Phan and Phan, 2009; Meng et al., 2008; Keskin et al., 2010;

Balbasi et al., 2011; Basha et al., 2009). Another and important advantage of biodiesel is its domestic origin that would help a country's dependency on imported petroleum (Keskin et al., 2008).
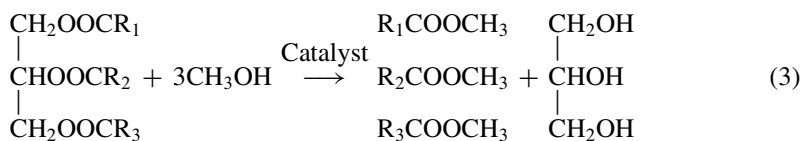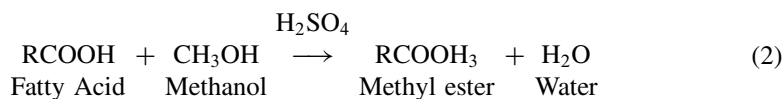
Biodiesel can be produced from a variety of vegetable oils, animal fats, and waste cooking oils. Countries produce biodiesel using vegetable oil, which they have more of. Biodiesel made from rapeseed oil is the most common biodiesel available in Europe, while soybean biodiesel predominates in the United States. In Malaysia and Indonesia, palm oil is used as a significant biodiesel source. In India and Southeast Asia, the jatropha tree is used as a significant fuel source (Demirbaş, 2008; Knothe and Van Gerpen, 2005; Van Gerpen, 2004).

Compared to diesel, the primary factor in preventing biodiesel's more widespread use is its high production price. In order to decrease the price of biodiesel, waste oils, which are easily available, have become resources for biodiesel production. Biodiesel production from waste oils is cheaper and environmentally beneficial, since evaluation these oils as an alternative fuels in vehicle engines protects the environment (Banarjee and Chakraborty, 2009; Patil et al., 2010; Wang et al., 2007).

Waste oils have a high amount of free fatty acids (FFAs). The waste oils that have rates of FFA smaller than 15% are classified as yellow grease and greater than 15%, they are classified as brown grease. Trap greases are very low-quality feedstocks obtained from an oil separator and their rate of FFAs can approach 100%. Because of the high FFA range, the use of waste oils to produce biodiesel has a negative impact on the reaction yield. When an alkali catalyst is added to these oils, the FFA reacts with the catalyst to form soap and water (Knothe and Van Gerpen, 2005; Marchetti and Errazu, 2008; Gürü et al., 2010) as shown in Eq. (1):

$$R - COOH + KOH \rightarrow R - COOK + H_2O. \tag{1}$$

Many researches were carried out to produce biodiesel from these waste oils. In these studies, two-step processes were used to remove the high FFA contents in these waste oils (Chongkhong et al., 2009; Berchmans and Hirata, 2008; Peng et al., 2008; El-Mashad et al., 2008). At the first step, acid catalyzed esterification is used to decrease the FFA content of the oil less than 1%. The second step, alkaline-catalyzed transesterification process, converts the products of the first step to biodiesel and glycerol (Gürü et al., 2009). These reactions are shown, respectively, in Eqs. (2) and (3):

$$
\begin{array}{c}
H_2SO_4 \\
RCOOH + CH_3OH \xrightarrow{\quad\quad} RCOOH_3 + H_2O \\
\text{Fatty Acid} \quad \text{Methanol} \quad\quad \text{Methyl ester} \quad \text{Water}
\end{array}
\tag{2}
$$

$$
\begin{array}{lll}
CH_2OOCR_1 & R_1COOCH_3 & CH_2OH \\
| & & | \\
CHOOCR_2 + 3CH_3OH \xrightarrow{\text{Catalyst}} R_2COOCH_3 + & CHOH \\
| & & | \\
CH_2OOCR_3 & R_3COOCH_3 & CH_2OH
\end{array}
\tag{3}
$$

The purpose of this study was to investigate the effect of various reaction parameters on esterification of waste cooking oils (WCO), such as methanol/waste cooking oils ratio, amount of acid catalyst, reaction time, and reaction temperature. Also, the physical properties of biodiesel and its blends were characterized for density, viscosity, acid value, flash point, sulphur content, copper strip corrosion, and calorific value.

2.   Materials and Method

The WCO, which contain high free fatty acids, was obtained from Cukurova University refectory's oil separator. This refectory serves 5,000 people every day and produces many WCO. In this refectory, waste water that comes from the refectory to the sewer system contains waste cooking oil. These waste cooking oils cause the sewer system's tubes to be plugged and cause other environmental problems. Therefore, an oil separator is used to separate waste oil from waste water. The oil inside the waste water is dissipated by utilizing the density difference, and contains the rest of the food, water, and detergent. The oil also contains a high rate of FFA owing to high temperatures and water during the cooking and the washing process. The oil separator drawing is shown in Figure 1.

The WCO were obtained from an oil separator and contain high FFA, and the range of FFA in WCO has been changed. So, the WCO have been collected for 6 weeks as a sample in a week. They were filtered to remove inorganic residues, then washed with pure water four times and dried. After these processes, the physical properties of WCO samples were designated. At the end, these samples were mixed together prior to the esterification. In Table 1, the physical properties of WCO samples are shown.

Methanol was used as alcohol in this process because it is the most widely used alcohol for biodiesel production, it is easy to process, and is relatively low cost (Çaylı and Küsefoğlu, 2008). Sulfuric acid was preferred as the catalyst because it gives very high yields in alkyl esters (Zullaikah et al., 2005). Solutions of sulfuric acid in methanol were prepared at room temperature. A flow diagram of the biodiesel production from trap grease process is shown in Figure 2.
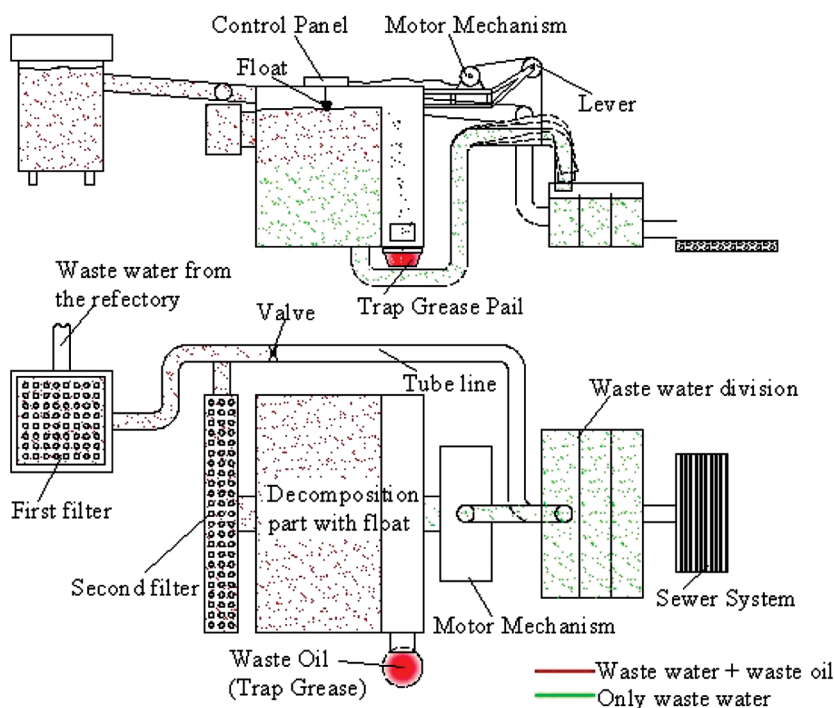
**Figure 1.** Oil separator drawing. (color figure available online)

Table 1
Physical properties of WCO samples

| Quality	Unit	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Average
Density	g/cm^3	0.909	0.908	0.911	0.910	0.909	0.909	0.909
Viscosity (40°C)	mm^2/s	25.52	27.32	29.96	25.58	30.04	33.82	28.70
Free fatty acid	%	68.05	71.26	62.73	65.09	64.02	59.75	65.15

The esterification reaction was carried out in a 1,000-ml glass flask equipped with a reflux condenser using tap water to condense methanol vapor, stirrer, and thermometer. The WCO fed into the reactor was preheated before the catalyst and the alcohol was added. After reaching the reaction temperature, the catalyst and the alcohol were adjoined in the reactor to start the reaction. Samples taken from the reactor were hanged for 8 h so that the catalyst would sink to the bottom. After the separation, samples were washed four times with pure water to remove the catalyst effect. Then samples were dried over 100°C to remove water content.

The molar ratio of alcohol, reaction temperature, catalyst amount, and reaction time were investigated to determine the best strategy for the esterification process. In order to determine the effect of the molar ratio on WCO conversion efficiency, reactions were conducted with 6 wt% sulphuric acid amount with methanol/WCO molar ratio at 3:1, 6:1, 9:1, 12:1 at 60°C and to determine the effect of catalyst amount on WCO conversion efficiency, the reaction was carried out with the optimum molar ratio 9:1 at 60°C with sulphuric acid amounts at 1, 3, 6, 9, and 12 wt%. The reactions were kept for each molar ratio and catalyst amount at 5, 30, 60, and 120 min to determine the effect of reaction time. Finally, the effects of reaction temperature on WCO conversion efficiency at 50, 60, 70, and 80°C were also experienced.

The analyzing of product samples was carried out at a fuel analysis laboratory in Cukurova University. A KYOTO DA-130 Portable Digital Density Tester (Kyoto Electronics Manufacturing Co., Ltd., Shanghai, China), TANAKA Flash Point Tester (Tanaka Scientific Limited, Tokyo, Japan), K 40091 Cinematic Viscosity Meter (Expotech, Houston, TX), Copper Strip Corrosion Tester (Koehler Instrument Company, New York), X-Ray Sulfur Analyzer (Tanaka Scientific Limited, Tokyo, Japan), and IKA WERKE Bomb
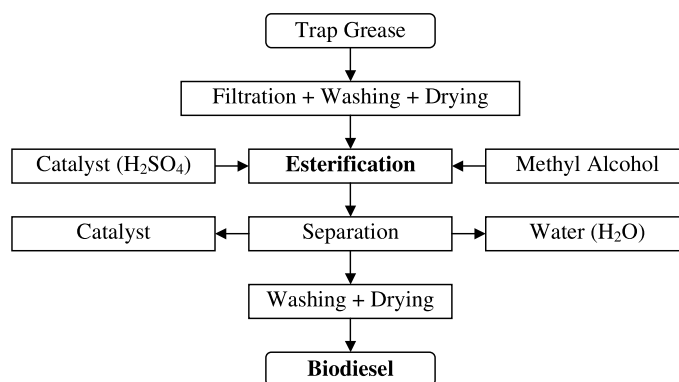
**Figure 2.** Flow diagram of biodiesel production from trap grease.
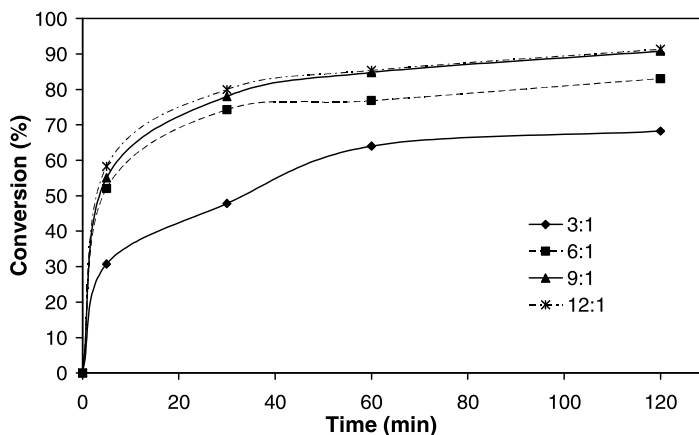
Figure 3. Effect of molar ratio on WCO conversion efficiency at a temperature of 60°C and 6 wt% sulphuric acid.

Calorimeter (IKA-Werke GmbH & Co. KG, Staufen im Breisgau, Germany) were used for analyzing the product samples. The acid value was determined with titration analyses.

3.   Results and Discussion

3.1.   Esterification of WCO with Methanol

3.1.1.   Effect of Methanol to Oil Molar Ratio. The molar ratio of alcohol to WCO is one of the most important factors that influence the conversion efficiency. The changes in conversion, specific gravity, and cinematic viscosity are shown, respectively, in Figures 3, 4, and 5. The conversions reached a maximum of 91.36% at the 12:1 molar ratio and 120 min. With further increase in molar ratio, the conversion efficiency more or less
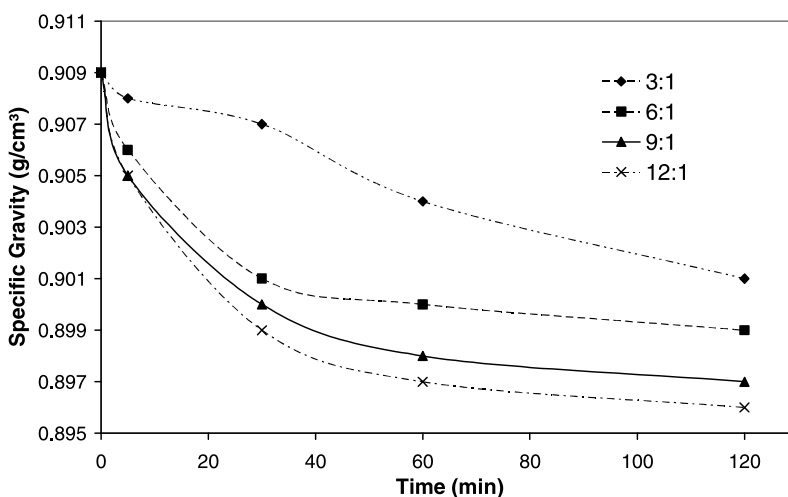
Figure 4. Effect of molar ratio on specific gravity at a temperature of 60°C and 6 wt% sulphuric acid.
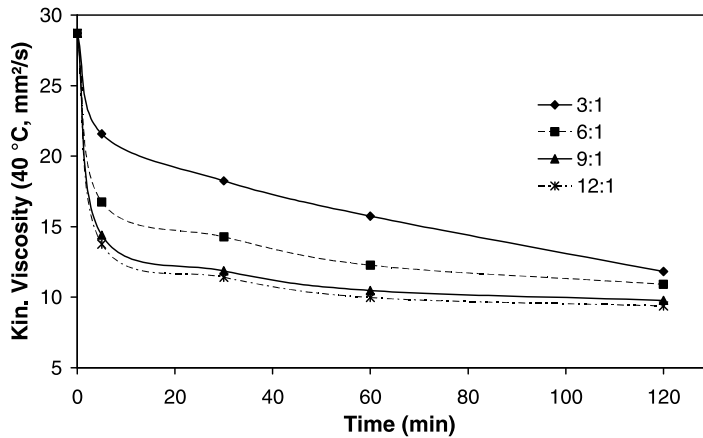
Figure 5. Effect of molar ratio on kinematic viscosity at a temperature of 60°C and 6 wt% sulphuric acid.

remained the same. The WCO conversion efficiency (90.84%) at 9:1 molar ratio was similar to the results obtained by 12:1 molar ratio. Considering that excessive methanol needs to remove from higher molar ratio, so 9:1 molar ratio maybe is more suitable in practical process. The specific gravity and viscosity decreased somewhat with increasing molar ratio. The specific gravity and viscosity were measured at 9:1 molar ratios and 120 min were, respectively, 0.897 and 9.78 mm^2/s. The optimum ratio in this study was in accordance with that obtained from other investigators (Demirbaş, 2008; Marchetti and Errazu, 2008; Peng et al., 2008; Lin et al., 2009).

3.1.2. Effect of Catalyst Amount. The catalyst amount is another important factor that affects the conversion efficiency. The effect of sulphuric acid amount on WCO conversion efficiency is presented in Figure 6. From the ranges 1–9 wt%, the conversion efficiency increased proportionally with increasing sulphuric acid amount. The maximum WCO
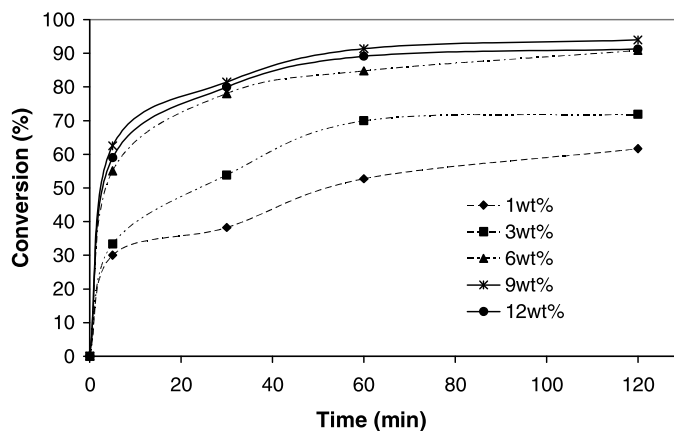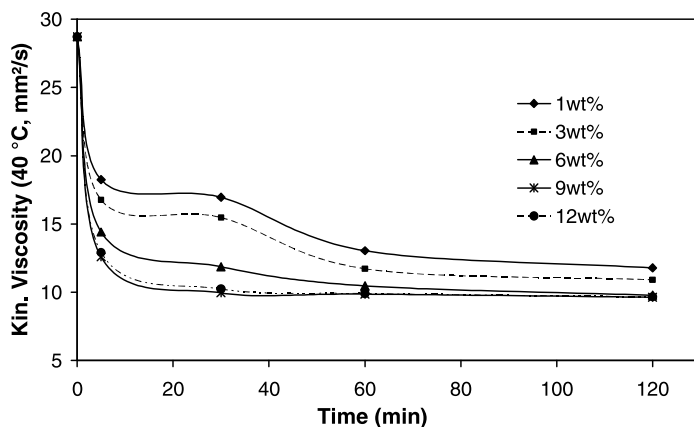

Figure 6. Effect of catalyst amount on WCO conversion efficiency at a temperature of 60°C and 9:1 molar ratio.
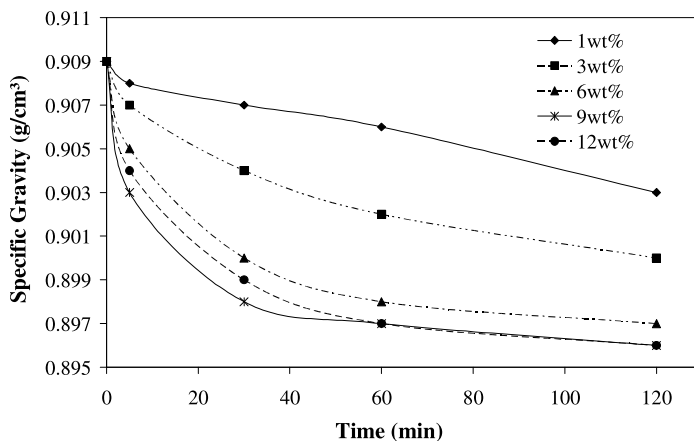
**Figure 7.** Effect of catalyst amount on specific gravity at a temperature of 60°C and 9:1 molar ratio.

conversion efficiency (93.98%) was observed at 9 wt% sulphuric acid amount. The addition of an excess amount catalyst gave rise to the formation of an emulsion, which increased the viscosity and led to the formation of gels (Lin et al., 2009). Thus, a sulphuric acid amount beyond 9 wt% was not necessary. These results are similar to the study of Marchetti and Errazu (2008). The changes in specific gravity and kinematic viscosity are shown, respectively, in Figures 7 and 8. The specific gravity and viscosity at maximum WCO conversion efficiency were 0.896 and 9.63 mm^2/s, respectively.

3.1.3. Effect of Reaction Temperature. Four different temperatures (50, 60, 70, and 80°C) were selected to determine the effect of temperature on conversion efficiency. Each reaction was run for 120 min with 9 wt% sulphuric acid catalyst and 9:1 molar ratio. The changes in the conversion efficiency are presented in Figure 9. The maximum conversion was observed at 60°C reaction temperature. The WCO conversion efficiency decreased

Figure 8. Effect of catalyst amount on cinematic viscosity at a temperature of 60°C and 9:1 molar ratio.
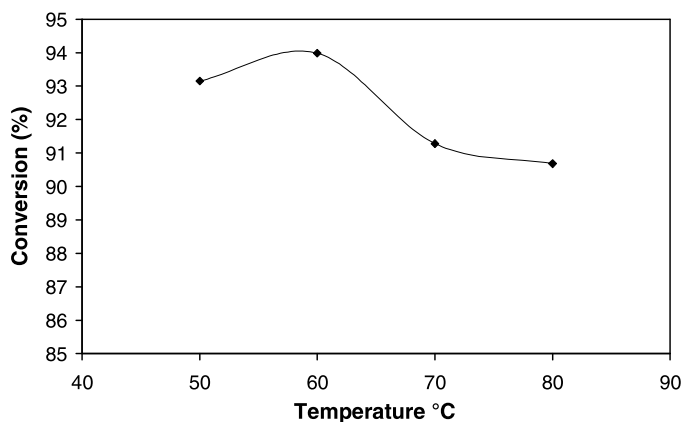
Figure 9. Effect of reaction temperature on WCO conversion efficiency at 9:1 molar ratio and 9 wt% catalyst amount.

beyond 60°C reaction temperatures. When the reaction temperature closes or exceeds the boiling point of methanol, the methanol will vaporize and form a large number of bubbles then inhibit the reaction (Meng et al., 2008). Although a reflux condenser was used in the experiment to avoid methanol losses, the WCO conversion efficiency significantly decreased at temperatures more than 60°C. Similar results were reported by Lin et al. (2009).

3.2. Characteristics of Biodiesel and Its Blends with Diesel

Biodiesel derived from WCO was analyzed at Cukurova University Fuel Analysis Laboratory. The chemical and physical properties of biodiesel and its blends with diesel are presented in Table 2. The biodiesel samples were compared according to EN590 standards for density, viscosity, acid value, flash point, sulfur content, copper strip corrosion, and calorific value. The B100 fuel had a density of 896 kg/m^3 and a viscosity of 9.88 mm^2/s, these values were higher than diesel. The higher flash point (96.8°C) compared with diesel is beneficial in the safety aspect, and the low sulfur content (0.0538 wt%) is the reason for the extremely low SO$_x$ emission. The acid value of B100 fuel was 3.92 and was higher than diesel. Because the WCO samples had a high range of free fatty acid, the products' acid value was not reduced. The calorific value of B100 fuel was smaller than diesel. The reduction in calorific value for the biodiesel compared to diesel was due to the presence of oxygen in the biodiesel (Phan and Phan, 2009).

4. Conclusions

Optimization of biodiesel production from WCO that had a high amount range of FFA has been investigated. WCO were obtained from an oil separator. Esterification process was carried out to biodiesel production by sulphuric acid catalyst. An acid type catalyst is preferred over basic catalyst in esterification of FFA to avoid saponification reaction. The optimum conditions were determined to be 9:1 molar ratio, 9 wt% acid catalyst amount, 60°C reaction temperature, and 120 min reaction time. The maximum conversion

Table 2

Chemical and physical properties of biodiesel and blends with diesel

Quality	Unit	B10	B20	B30	B40	B50	B70	B100	Diesel	EN590
Density	kg/m^3	836	843	850	856	863	878	896	829	820–860
Viscosity (40°C)	mm^2/s	2.4	3.2	3.91	4.78	5.63	7.32	9.88	2	2.0–4.5
Acid value	mgKOH/g	0.27	0.48	1.07	1.58	2.03	2.83	3.92	0.05	—
Flash point	°C	63.5	64.5	65.4	66.5	68.5	74.5	96.8	62.5	Min 55
Sulfur content	wt%	0.0813	0.0770	0.0706	0.0672	0.0620	0.0602	0.0538	0.0826	Max 0.2
Copper strip corrosion	—	1a	1a	1a	1a	1a	1a	1a	1a	1
Calorific value	kJ/kg	44,016	43,271	42,485	41,719	41,139	40,272	38,913	44,717	—

efficiency was observed to be 93.98% at these conditions. The biodiesel was mixed with diesel in different volumetric ratios and their characteristics were observed. The samples were compared to each other according to EN590 standards. The results showed that the blend down 30% vol. could be applied in engines without major modification. The present study showed that WCO can be used as an addition fuel to diesel, so environmental effects of these waste oils can be solved.

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