Article

Esterification and Deacidification of a Waste Cooking Oil (TAN 68.81 mg KOH/g) for Biodiesel Production

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Abstract: Oils with high content of free fatty acid (FFA) can be treated by acid esterification where an alcohol reacts with the given oil in the presence of acid catalyst. The investigated parameters include methanol to oil ratio, temperature and amount of catalyst. The optimum conditions for acid esterification which could reduce FFA content in the feedstock to less than 1.88% (acid value 3.76 mg KOH/g waste cooking oil) were 50 °C, 20% methanol to oil ratio (by volume) and 0.4 vol.% H_2SO_4 after 5 h. However, oil with an acid value of more than 1 mg KOH/g oil cannot meet the alkaline catalyzed transesterification conditions. Under the conditions of NaOH concentration 0.5 N, excess alkali 15%, 60 °C, 40 min, the FFA removal rate for deacidification reached 77.11% (acid value 0.86 mg KOH/g esterified oil). The acid value of deacidification product was reduced below 0.86 mg KOH/g esterified oil, thus meeting the base-catalyzed trans-esterification conditions.

Keywords: biodiesel; deacidification; esterification; free fatty acids; waste cooking oil

1. Introduction

Among various alternative fuels produced from renewable resources, biodiesel, which is well known as a replacement for the traditional petroleum diesel fuel [1], is currently becoming a fast-growing market product [2–4]. It is composed of mono-alkyl esters of long chain fatty acids derived from plant and animal oils and fats by transesterification with short carbon alcohols such as methanol. Biodiesel is a renewable, biodegradable and nontoxic fuel. It can be used in existing compression-ignition engines with little or no modifications. The use of pure biodiesel in the transport sector lowers the soot emissions by 60%, carbon monoxide and hydrocarbons by 50% and carbon dioxide by 80%, respectively. Nevertheless, emissions of NO_x may vary by ±10% depending on the engine's combustion characteristics [5]. No sulfur dioxide emissions occur because there is sulfur in biodiesel due to its vegetable origin [6].

However, biodiesel is currently not cost competitive with conventional diesel fuel due to its high raw material and production costs [7]. To reduce the cost of biodiesel, in general, the selection of oil feed is very critical. The oil feeds containing high free fatty acids (FFA), such as waste fats or non-edible type oils, are much cheaper than vegetable oils, such as soybean or rapeseed oil [8–10]. In China, biodiesel is mainly produced from non-edible and waste oils and fats such as tung oil, *Jatropha curcas L.* oil, waste cooking oil (WCO), trapped grease, soapstock and acidified oil [11]. The production of biodiesel from WCO is an approach to lower biodiesel production costs [12,13]. On the other hand, the use of WCO as a biodiesel feedstock can also avoid the sensitive "food *versus* fuel" debate [14]. However, WCO contains a lot of FFA, and since FFA form soaps with alkali catalysts during transesterification, they must be removed prior to the transesterification process. Therefore, the FFA in WCO was often esterified first using acid-catalysts. Then the fat in the WCO is transesterified by base-catalysis [15,16]. FFA react with alcohol under acid catalysis, producing ester and water. This reaction is described in the following Equation (1) [17,18]:

$$R_1 - COOH + R_2 - OH \xleftarrow{\text{catalyst}} R_1 - COO - R_2 + H_2O \qquad (1)$$

Liquid acids, such as sulfuric acid and hydrochloric acid, are usually used as acid-catalysts, the former being the most commonly used catalyst in esterification process [19].

When the efficiency of esterification is relatively low, residual FFA produces soaps due to the alkali catalysis, making the separation of biodiesel and alcohol difficult, and simultaneously decreasing the final yield of biodiesel. WCO transesterification catalyzed by alkali only becomes possible when the acid value of oil is less than 1 mg KOH/g oil. Higher percentages of FFA in the oil reduce the yield of the transesterification process. In fact, for oil with high FFA levels, the first esterification cannot meet the alkali catalyzed reaction conditions, which requires a second esterification in order to reduce acid value to less than 2 mg KOH/g oil [20]. The work done by Park [21] also reached a similar conclusion. Furthermore, the acid value was still more than 1.5 mg KOH/g after washing esterified oil (EO) with 1 N NaOH. To reduce the acid value of EO to less than 0.5 mg KOH/g, another washing procedure is required. The EO will have some FFA and can be further deacidified by alkali refining. The deacidification of alkali refining process is accomplished by the addition of an alkali to EO, thereby precipitating the FFA as soapstock; which is then removed by mechanical separation from the EO. The

alkali most often used for neutralization is caustic soda (sodium hydroxide) [22], so an economical, integrated deacidification procedure would be valuable [23].
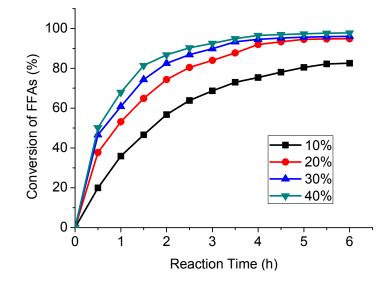
In this work, the direct esterification reaction of the FFA in the presence of WCO was studied. Sulfuric acid was used as catalyst and methanol was used as alcohol. The most relevant variables for the reaction were methanol to WCO ratio, amount of catalyst in relation to the amount of WCO and reaction temperature. The deacidification process of alkali neutralization has also been investigated for esterified WCO oil of varying FFA with respect to the effects of variables including the concentration of alkali, excess alkali, temperature and time on the reduction of FFA. Details of this work are described in the sections that follow.

2. Results and Discussion

2.1. Effect of Methanol/WCO Ratios on the Esterification

The ratio of methanol to WCO is one of the important factors that affect the conversion efficiency as well as production cost of biodiesel [3]. Theoretically, the esterification reaction requires one mole of methanol for each mole of FFA. However, in practice, the methanol should be in excess to drive the reaction towards completion as the esterification of FFA with methanol [*cf.* Equation (1)] is reversible. In order to study the effect of methanol/WCO volume ratios on esterification, different experiments were carried out using different methanol/WCO volume ratios of 10%, 20%, 30% and 40%, as shown in Figure 1. The FFA conversion increased from 80.43% to 94.54% when the methanol/WCO volume ratio was increased from 10% to 20% after a reaction time of 5 h under the conditions of 0.4% sulphuric acid and a reaction temperature of 50ºC. The FFA conversion increased only slightly from 94.54% to 95.65% when the methanol/WCO volume ratio rose from 20% to 30%. With further increases in volume ratio there is little improvement in the conversion efficiency. Therefore, the optimized methanol/WCO volume ratio was determined to be 20% in this reaction system.

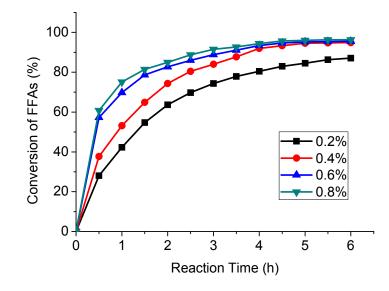**Figure 1.** Effect of methanol/WCO volume ratios on the esterification.

According to the curves in Figure 1, the conversion efficiency of FFA increased with the reaction time for a given methanol/WCO ratio. At the beginning of the reaction, the conversion of FFA

increased rapidly with reaction time. As the reaction proceeded, the forward reaction rate was reduced while the reverse reaction rate increased.

2.2. Effect of the Amount of Sulphuric Acid on the Esterification

The amount of sulphuric acid used in the process also affects the conversion efficiency of the process. The catalyst amount was varied in the range of 0.2–0.8 vol.% for four different values of sulphuric acid (0.2, 0.4, 0.6 and 0.8 vol.%). These percentages are volume fractions of the oil supplied for this reaction. The effects of the catalyst amount on the conversion efficiency were investigated as illustrated in Figure 2. The FFA conversion increased rapidly from 85.54% to 94.54% when the catalyst amount rose from 0.2% to 0.4% after a reaction time of 5 h under the conditions of methanol/oil volume ratio 20%, and a reaction temperature of 50 °C. In addition, it is noted that during the present experiments, that excess addition of sulphuric acid made the color of the product darken [3]. Therefore, the catalyst dosage should be 0.4 vol.%.

Figure 2. Effect of the amount of sulphuric acid on the esterification.

2.3. Effect of Reaction Temperature on the Esterification

The effect of temperature on the esterification of WCO was investigated by carrying out the experiment at a fixed methanol/WCO ratio of 20% and amount of sulphuric acid of 0.4% with a reaction time of 6 h. The experimental temperature was in the range from 40 °C to 65 °C, as shown in Figure 3. It was observed that increasing the reaction temperature had a favorable influence on the degree of esterification. With an increase in temperature, the conversion rose at a faster rate. At higher reaction temperatures, however, there was a chance of methanol loss and product darkness increased. High reaction temperatures also increased the production cost of biodiesel. The optimum temperature for this reaction is found to be 50 °C. Due to the lower boiling point (64.5 °C), methanol vaporized in the reaction solution, which not only makes the reaction system pressure rise, but also affects the mass transfer in the reaction mixture, and then reduces the reaction rate. Hence, the general esterification reaction temperature is controlled at about 50 °C [24].
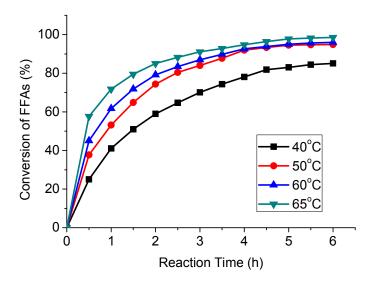
Figure 3. Effect of reaction temperature on the esterification.

2.4. Effect of the Alkali Concentration on the Deacidification

The alkaline reagent, sodium hydroxide concentration at the range of 0.1–1.0 N is used in the present experimental analysis. The effect of the concentration of alkali on the deacidification is shown in Table 1. The maximum conversion efficiency is achieved at 0.5 N of NaOH. With further increases of the amount of alkaline reagent the conversion increased only slightly. This may be attributed to the formation of alkali lye scattered in large droplets accompanying with small surface area, thus affecting the interface reaction rate. Too low a sodium hydroxide concentration results in poor stratification between oil and soap, so that the small soap particles make the separation difficult. In this work, the optimal concentration of alkali to reduce FFA was 0.5 N.

Table 1. Effect of alkali concentration, excess alkali, temperature and time on the deacidification.

Alkali concentration (N)	Conversion (δ, %)	Excess Alkali (%)	Conversion (δ, %)	Temperature (°C)	Conversion (δ, %)	Time (min)	Conversion (δ, %)
0.1	56.61	5	64.89	30	33.35	10	59.81
0.3	67.87	10	71.46	40	48.12	20	67.65
0.5	77.11	15	77.11	50	64.76	30	72.33
0.8	78.36	20	78.35	60	77.11	40	77.11
1	78.52	25	78.79	70	76.79	50	74.54

2.5. Effect of Excess Alkali on the Deacidification

In addition, a part of the alkali was consumed in the saponification of neutral oil. Therefore, a large excess of alkali is used to shift the equilibrium far to the soap. Effect of five different levels of excess alkali (5%, 10%, 15%, 20% and 25%) were also studied. The operational temperature was 60 °C and the reaction time was 40 min while the concentration of alkali was kept constant at 0.5 N. The results are displayed in Table 1. When the excess alkali increased from 5% to 15%, the acid removal rate of esterification product quickly went from 64.89% to 77.11%. Since the reaction is an equilibrium reaction, increasing the reactants would promote the equilibrium towards the product. When the excess

alkali increased from 15% to 25%, the reaction took place smoothly with the highest acid removal rate of esterification product of 78.79%.

FFA in oil could not be neutralized completely with the lower alkali dosage, and the generated fine soap particles cannot be separated well. On the other hand, with an excessive amount of alkali, the neutral oil was saponified, consequently, the esterification products are lost. In the deacidification step of the alkali refining process, there is a considerable oil loss due to the hydrolysis of neutral oil by caustic. Besides, loss of oil also occurs in the form of occlusion in soapstock. The soapstock can hold as much as 50% of its weight of neutral oil, thereby reducing the overall yield of refined product [25]. Therefore, the optimized alkali excess quantity is 15%.

2.6. Effect of Temperature on the Deacidification

The effect of alkaline refining temperature on the deacidification was studied by varying the temperature in the range from 30 °C to 70 °C, while the concentration of NaOH was fixed at 0.5 N, excess alkali at 0.3% and 40 min reaction time as shown in Table 1. From the data, it is clear that the acid removal rate of esterification product increased proportionally with reaction temperature until optimum temperatures of 60 °C and 70 °C were reached, giving optimum acid removal rates of 77.11% and 76.79%, respectively. It would appear from the curve that the soap formed surrounds the sodium hydroxide solution globules and retards absorption at low temperature, but triglyceride and methyl esters react with the alkali at high temperature. Hence, the alkaline refining reaction temperature of deacidification process should not be higher than 60 °C in order to avoid unnecessary decomposition of triglyceride and methyl esters.

2.7. Effect of Time on the Deacidification

Table 1 shows the effect of time on the deacidification using NaOH at the concentration 0.5 N, excess alkali 0.3%, 60 °C. The results indicate that the acid removal rate was influenced by the time. With reaction times from 10 min to 40 min, the acid removal rate of esterification product increased from 59.81% to 77.11%; however, the acid removal rate of esterification product decreased from 77.11% to 75.54% when the reaction time rose from 40 to 50 min. Therefore, the optimized reaction time was determined set as 40 min in this reaction system.

3. Experimental Section

3.1. Materials

The WCO with an acid value of 68.81 mg KOH/g WCO was supplied by Shandong Beite Bioenergy Company (Zibo, China). The WCO was filtered before use to remove impurities. Water content was detected by the Karl Fisher water tester with a sensitivity of 500 ppm (KF-1A, Shanghai Precision and Scientific Instrument Co., Ltd., Shanghai, China). Potassium hydroxide, methanol, sulphuric acid, sodium hydroxide, and other chemicals were reagent grade and used without any further purification.

3.2. Esterification Procedure

Esterification was performed at atmospheric pressure in a three-necked batch reactor (150 mL) equipped with a reflux condenser and a mechanical stirrer. The reactor was heated with a heating jacket and a thermocouple was inserted in the reactor to measure the reaction temperature. A certain amount of the WCO was fed into the batch reactor. Then the desired amounts of methanol and sulphuric acid were added into the batch reactor and the reaction began under the required conditions. The basic reaction conditions were oil amount 50 mL, methanol/oil volume ratio 20%, catalyst amount 0.4%, reaction temperature 50 °C and reaction time 6 h. Samples were withdrawn at half-hour intervals. After centrifuging, the methanol layer was drained off and the biodiesel layer was left. Then the biodiesel layer was washed with deionized water three times. The water content of the samples was decreased to 0.05% by vacuum evaporation. The acid value of reaction system was determined so as to calculate FFA conversion.

3.3. Determination of the Acid Value and FFA Conversion

The acid value of the sample was determined by a standard titration method (China Standard—Animal and Vegetable Fats and Oils-Determination of Acid Value and Acidity GB/T5530-2005). The brief steps were as follows: sample (0.25 g) was added to some amount of neutralized ethanol and was fully dissolved by heating. Phenolphthalein (0.5 mL) was used as an indicator. The sample was then titrated with 0.1 MKOH solution. The acid value was calculated using Equation (2):

$$S = \frac{56.1 \cdot V \cdot c}{m} \tag{2}$$

where S is the acid value (mg KOH/g WCO); c is the concentration of the KOH used for titration (mol/L); V is the volume of KOH employed for titration (mL); m is the weight of the sample taken to be analyzed (g).

The conversion of FFAs is defined as the change of acid value before and after reaction of the oil with respect to acid value of the initial oil. It can be determined from the following Equation (3):

$$\eta(\%) = \frac{S_0 - S_i}{S_0} \tag{3}$$

where the S_0 refers to initial acid value; and S_i refers to the acid value at some reaction time, respectively.

3.4. Deacidification

Some of the esterified samples were further deacidified by the conventional alkali neutralization process. Deacidification of alkali neutralization process was conducted in a three-necked flash (150 mL) fitted with a mechanical stirrer, and a thermometer inlet. The reactor was heated by a temperature controlled mantle. The EO sample was mixed with sodium hydroxide solution slowly by stirring at a certain temperature. The basic reaction conditions were EO amount 20 g, NaOH concentration 0.5 N, excess alkali 15%, reaction temperature 60 °C and reaction time 40 min. At the scheduled time, deionized water with the same temperature as the oil and 5% amount of oil mass were added into the oil and soap mixture to promote the coagulation and sedimentation. Soap stock was removed by

centrifugation at 6000 rpm. After washing to neutrality with deionized water, the washed oils were dried under vacuum. FFA deacidification rate of the EO was calculated by the following Equation (4):

$$\delta(\%) = \frac{S_p - S_d}{S_p} \times 100\% \tag{4}$$

where δ refers to FFA removal rate (%); S_p refers to acid value of esterification oil (mg KOH/g); S_d refers to acid value of deacidification oil (mg KOH/g).

4. Conclusions

In the present investigation, sulfuric acid esterification was studied to reduce the FFA content of WCO. Optimum esterification conditions were found to be 50 °C, 20% methanol to oil ratio and 0.4 vol.% sulphuric acid. However, the acid value of EO with 3.76 mg KOH/g oil cannot meet the alkaline catalyzed transesterification condition. The deacidification of the alkali refining process reduced the FFA of EO to the desired level. The acid value of the deacidification product was reduced below 0.86 mg KOH/g EO under the conditions of NaOH concentration 0.5 N, excess alkali 15%, temperature 60 °C, and time 40 min, thus meeting the base-catalyzed transesterification conditions.

Acknowledgments

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