

Comparison of two different processes to synthesize biodiesel by waste cooking oil

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Abstract

The traditional acid and the new two-step catalyzed processes for synthesis of biodiesel expressed as fatty acid methyl ester (FAME) were comparatively studied to achieve an economic and practical method for utilization of waste cooking oil (WCO) from Chinese restaurants. WCO samples with the acid value of 75.92 ± 0.04 mgKOH/g mixed with methanol were catalyzed under 95°C for various reaction time, followed by methanol recovery under vacuum (10 ± 1 mmHg) at 50°C with a rotational evaporation. FAME analyzed by gas chromatography (GC) was obtained directly from sulfuric acid catalyzed reaction in the traditional acid method, whereas in the two-step method it was produced from ferric sulfate (2.0%) catalyzed reaction followed by alkali (1.0% potassium hydroxide) transesterification. The conversion of free fatty acids of WCO into FAME in the two-step method was 97.22% at the reaction time of 4 h, mole ratio of methanol to TG of 10:1, compared in the acid method with 90%, 10 h, and 20:1, respectively, showing much higher catalyzed activity of ferric sulfate. This new two-step process showed advantages of no acidic wastewater, high efficiency, low equipment cost, and easy recovery of catalyst compared with the limitations of acidic effluent, no reusable catalyst and high cost of equipment in the traditional acid process.

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1. Introduction

The price of fossil diesel is soaring in the recent 2 years and it will be exhausted some day. Thus, looking for an alternative way to develop a substitute of diesel is an imperious task for humans. Biodiesel, defined as “a substitute for, or a additive to diesel fuel that is derived from the oils and fats of plants and animals” [1] or mono-alkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat (ASTM), is becoming popular in the markets of developed countries as well as developing ones. The European Union has set an objective to secure for motor biofuels a market share of 20% of total motor fuel consumption by 2020. Fossil diesel blended with 20% of biodiesel produced by the soybean oil is available in the US market now [2]. Developing renewable energy is the national strategy of China that has limited fossil oil deposit but needs more energy than before [3].

The main advantages of using this alternative fuel are its renewability, better quality of exhaust gas emissions, its biodegradability and, given that all the organic carbon present is photosynthetic in origin, it does not contribute to a net rise in the level of carbon dioxide in the atmosphere if all of the energy inputs for the biodiesel production are non-fossil-based, and consequently to the greenhouse effect [4].

The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters (i.e., biodiesel) and glycerol. Methanol is the most commonly used alcohol due to its low cost [1,5].

From the view of chemical reaction, refined vegetable oil is the best start material to produce biodiesel because the conversion of pure triglyceride (TG) to fatty acid methyl ester (FAME) is high and the reaction time is relatively short. Nevertheless in China, the biggest developing country with population of over 1.3 billion, the limited refined edible oil must meet the need of consumers first. Waste cooking oil (WCO), if no suitable treatment available, would be discharged to cause the environment pollution. But now, the WCO is

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collected by environmental protection agency authorized by local government in the main cities of China. It is estimated that the WCO collected in Guangzhou, the third biggest city in China, is over 20 000 t each year. This collected material is a good commercial choice to produce biodiesel due to its low cost.

Biodiesel produced by transesterification reactions can be catalyzed with alkali, acid or enzyme. But the former two types have received more attention due to their short reaction time and the low cost compared with the later. Some studies show that the lipase is very sensitive to methanol in enzyme-catalyzed process, so methanol in the reaction system should be kept at quite low concentration to ensure the activity of the enzyme [6–8]. It took 34 h to convert 97.3% of TG of the refined vegetable oil to FAME in a two-step batch enzymatic process. While the WCO was used as a reactant, the conversion of the oil was only 90.4% by a three-catalyzed process with 48 h [6].

Chemical catalyzed processes including alkali and acid ones are more practical, compared with the enzymatic method. Alkali process can achieve high purity and yield of biodiesel product in a short time (30–60 min) [9–11]; however, it is very sensitive to the purity of reactants. Only the well-refined vegetable oil with less than 0.5% free fatty acid (FFA) can be used as the reactant in this process [12]. The high cost of raw material is the major obstacle to its commercialization. When treated with the WCO with more than 10% FFA, acid process is preferred for commercial use due to its simplicity [12–14].

In addition, the combined process with acid catalyzed pretreatment was developed to improve the yield of biodiesel by the WCO. The pretreated step of this process was to esterify the FFA with methanol by acid catalysis. When the FFA content was lower than 0.5%, the sulfuric acid was drained and the solid alkali was introduced into the system to complete the transesterification [12,15]. However, long reaction time, no recovery of catalyst and high cost of reaction equipment were disadvantages of this process [16].

To overcome the disadvantages of acid catalyzed process or pretreatment, the homogeneous Lewis acid catalyst (carboxylic salts) was used [17]. However, the reaction temperature was too high ($\leq 200^\circ\text{C}$), and the conversion ratio was relatively low ($\leq 90\%$).

In the current study, a comparative study on preparation of biodiesel from the WCO by two different processes was investigated. One process was traditional acid catalyzed one, in which the synthesis of biodiesel was catalyzed by sulfuric acid, but the other process was a new two-step catalyzed one. The mechanism of this new two-step catalyzed process for the preparation of biodiesel was shown in Fig. 1. At the first step, ferric sulfate was introduced to catalyze the esterification reaction in which the

FFA in the WCO reacted with methanol. The ferric sulfate that had very low solubility in the oil was separated from the liquid after the methanol recovery, and could be recovered by ashing process. At the second step, potassium hydroxide was added to catalyze the transesterification reaction in which triglyceride (TG) reacted with methanol. Without wastewater, reusable catalyst and low cost of reaction tank, this two-step catalyzed process exhibits potential application in the biodiesel industry.

2. Methods

2.1. Materials

WCO with acid value of 75.92 ± 0.04 mgKOH/g was provided by a local company that collected the WCO from restaurants by the authority of local government. Non-oil components of the WCO were removed by separation.

2.2. Acid catalyzed process

2.2.1. Preparation of biodiesel by sulfur acid catalysis

Extensive preliminary experimentation with the WCO samples indicated that it was most efficient to fix reaction temperature at 95°C . Stirring was not needed because boiling was sufficient. The acid catalyzed process included six levels of reaction time, 1, 2, 3, 4, 6, 8, 10 h; five levels of methanol to TG in mole ratio, 10, 12, 16, 20, 24; four levels of catalyst (sulfur acid), 3, 4, 5, 6 (% w/w, WCO).

Each 40 g sample mixed with methanol and sulfur acid was boiled at 95°C for a specified period, then excess of methanol was recovered under vacuum (10 ± 1 mmHg) at 50°C with a rotational evaporator, and the mixture was left to settle to separate into two layers. The upper oil layer was the FAME (crude biodiesel) and some unreacted triglyceride, and the down layer was sulfur acid and glycerol. Crude biodiesel was taken to analyze the purity by gas chromatography (GC).

2.2.2. Analysis of conversion of WCO

After each reaction, the crude biodiesel was taken to analyze the purity by GC. Lauric acid methyl ester was added as a reference into the crude biodiesel and the samples were analyzed by a GC, equipped with a capillary column (SPBTM-5, 30 m \times 0.32 mm \times 0.25 μm) and a flame ionization detector (FID). Nitrogen was used as the carrier gas. The injection was performed in split mode with a split ratio of 80:1. The analysis of biodiesel for each sample was carried out by dissolving 0.5 g of biodiesel sample and 0.05 g of lauric acid methyl ester into 10 ml of *n*-hexane and injecting 1 μl of this solution in the GC. The purity of crude biodiesel was calculated based on the area of FAME over the reference by the following equation:

$$\text{Purity}(\%) = \left(\frac{\text{area of FAME}/\text{area of reference} \times \text{weight of reference}}{\text{weight of crude biodiesel}} \right) \times 100$$

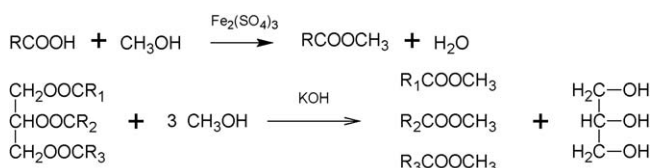


Fig. 1. Mechanism of synthesis biodiesel by two-step catalyzed process.

Purity of crude biodiesel refers to the conversion of WCO into FAME in each performance.

2.3. Two-step catalyzed process

2.3.1. Ferric sulfate-catalyzed methanolysis of WCO

The experiment plan involved six levels of reaction time, 0.25, 0.5, 1, 2, 3, 4 h; seven levels of catalyst (ferric sulfate), 0, 0.2, 0.5, 1, 2, 3, 4 (% w/w, WCO); five levels of methanol to TG in mole ratio, 3, 5, 7, 8, 10.

Each 40 g sample mixed with methanol and ferric sulfate was boiled for a specified period, then excess of methanol was recovered under vacuum (10 ± 1 mmHg) at 50°C with a rotational evaporator, and the mixture was left to settle to separate into two layers. The upper oil layer was the FAME (biodiesel) and unreacted triglyceride that was subjected to the second step transesterification and the down layer was water with ferric sulfate.

The conversion of FFA in the WCO into FAME was calculated from the mean of acid value (AV) of the oil layer by the following equation:

$$\text{Conversion}(\%) = \left(1 - \frac{\text{AV}_{\text{OL}}}{\text{AV}_{\text{WCO}}}\right) \times 100,$$

where OL and WCO refers to oil layer and waste cooking oil, respectively.

2.3.2. Recovery of catalyst

The down layer of ferric sulfate mixture after methanol recovery of each performance was collected in an ashing crucible, then it was ashed at 460°C for 5 h in a Muffle furnace to remove the organic impurities. The recovered ferric sulfate by the ashing process was added to reaction system to catalyze the methanolysis of WCO at the following optimal condition: reaction time of 4 h, catalyst of 2%, mole ratio of methanol to TG of 10:1, and reaction temperature of 95°C . The AV of the oil layer of the recovered ferric sulfate catalyzed was compared with that of the fresh one catalyzed. After reaction, the recovered ferric sulfate was also reclaimed by ashing. The recovery ratio of catalyst was calculated by the amount of recovered one over the fresh one.

2.3.3. Alkali catalyzed transesterification of WCO

The collected oil layer was transferred to a 250 ml round bottom one neck flask, then the six times of stoichiometric amount of methanol required for total conversion of triglyceride and 1.0% of potassium hydroxide were added. The mixture was reacted for 1 h at 65°C . The excess of methanol was recovered under vacuum (10 ± 1 mmHg) at 50°C with a rotational evaporator, then the mixture was left to settle to separate into two layers. The upper layer was the FAME (crude biodiesel) with lighter color and the down layer was the glycerol. The crude biodiesel was washed by 10% of water at 80°C to remove soap which was produced by reaction of the alkali and FFA. The wet crude biodiesel was dried under vacuum (5 ± 1 mmHg) at 90°C with a rotational evaporator for 1 h.

2.3.4. Analysis of biodiesel

The analysis of biodiesel for each sample was carried out by dissolving 0.5 g of biodiesel sample and 0.05 g of lauric acid methyl ester into 10 ml of *n*-hexane and injecting 1 μl of this solution in GC, with the same conditions as ones in acid method.

2.3.5. Distillation of FAME

The distillations were performed in a 500 ml round bottom one neck flask. The equipment includes a temperature controller, a receiver flask connected to a vacuum gauge and a condenser. A pump connected to the condenser provided vacuum. The dried crude biodiesel was fed to the flask; the vacuum was adjusted to 40 ± 5 mmHg. The first distillate fraction of FAME was collected at 180°C , and the distillation was terminated when no more distillate was appeared. The weights of feed, residue and distillate were determined to calculate the production rate of distillation.

3. Results and discussion

3.1. Acid catalyzed process for biodiesel

3.1.1. Effect of reaction time on WCO conversion

Effect of reaction time on the WCO conversion is shown in Fig. 2. The conversion of WCO into FAME catalyzed by sulfur acid can be divided into three phases. At the first phase, 26.8% of WCO (mainly FFA) was converted into biodiesel within 1 h. FFA is easier to react with methanol than TG because of its relatively simple structure. At the second phase, from reaction time of 1–6 h, TG plus some remained FFA reacted with methanol to produce biodiesel and glycerol. The reaction rate in this phase was lower than that of the first one since TG had some space resistance to react with methanol. At the third phase, after 6 h reaction, a majority of TG and most of FFA were converted into biodiesel, so the reaction approve to equilibrium and the rate was quite slow.

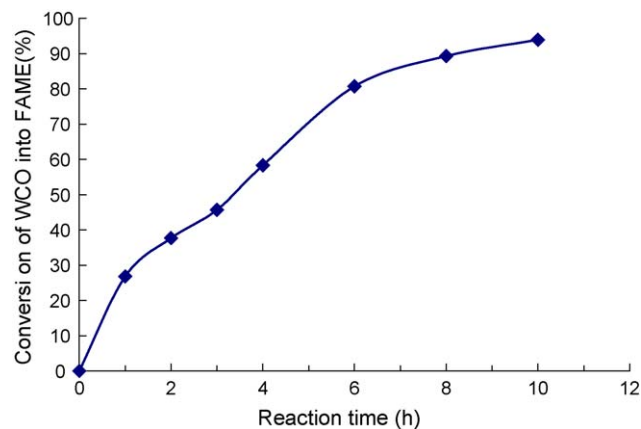


Fig. 2. Effect of reaction time on the conversion of WCO into FAME. Reaction temperature 95°C , amount of sulfur acid 4% (w/w, WCO) and methanol to TG in mole ratio 16:1. WCO, waste cooking oil; FAME, fatty acid methyl ester.

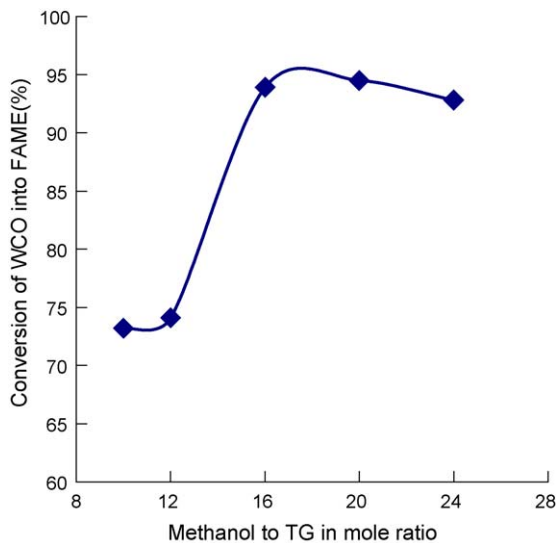


Fig. 3. Effect of methanol to TG in mole ratio on the conversion of WCO into FAME. Reaction temperature 95 °C, reaction time 10 h and amount of sulfur acid 4% (w/w, WCO). WCO, waste cooking oil; FAME, fatty acid methyl ester.

3.1.2. Effect of mole ratio of methanol to TG on WCO conversion

Fig. 3 shows the effect of mole ratio of methanol to TG on the WCO conversion into FAME. When methanol to TG in mole ratio exceeded 16, the conversion of WCO increased rapidly. Acid catalyzed process needs more excess of methanol than alkali catalyzed one; even mole ratio of methanol to TG over 30 is adopted to improve the yield of biodiesel [12]. However, when mole ratio exceeded 20, the conversion decreased slightly for the dilution of catalyst by the much excess of methanol.

3.1.3. Effect of amount of catalyst on WCO conversion

High amount of sulfur acid can accelerate the reaction of transesterification at right conditions (Fig. 4). When the mole ratio of sulfur acid to FFA was 5, the soapstock that was mainly fatty acid sodium salts was converted into biodiesel with 10 min at 35 °C [20]. In this experiment, the conversion of WCO

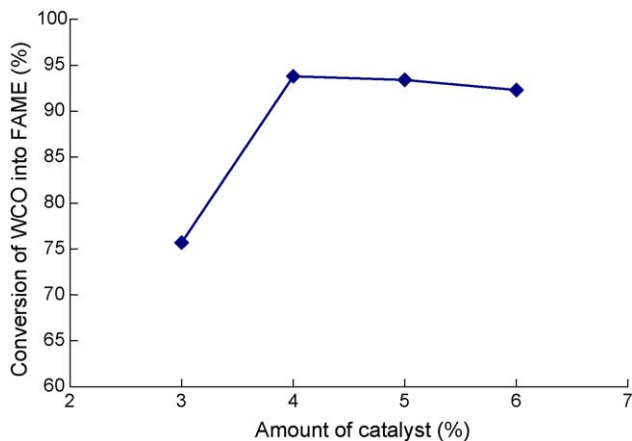


Fig. 4. Effect of amount of catalyst (sulfur acid) on the conversion of WCO into FAME. Reaction time 95 °C, reaction time 10 h and methanol to TG in mole ratio 16:1. WCO, waste cooking oil; FAME, fatty acid methyl ester.

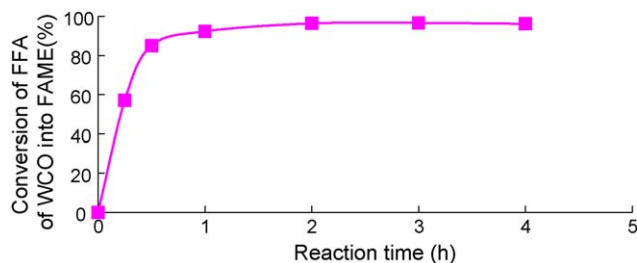


Fig. 5. Effect of reaction time on the conversion of FFA of WCO into FAME. Reaction temperature 95 °C, amount of ferric sulfate 2.5% (w/w, WCO), and mole ratio of methanol to TG 10:1. FFA, free fatty acid; WCO, waste cooking oil; FAME, fatty acid methyl ester.

increased with the increment of amount of sulfur acid within 4%. When the amount of sulfur acid exceeded 4%, the conversion of WCO didn't increase with the amount of catalyst. Although the amount sulfur acid was somewhat positive to the transesterification, the more sulfur acid added, the more byproducts and acidic effluent produced.

3.2. Two-step catalyzed process for biodiesel

3.2.1. Ferric sulfate-catalyzed methanolysis of WCO

3.2.1.1. Effect of reaction time on FFA conversion. Ferric sulfate can catalyze methanolysis of FFA but not TG, so the acid value can be calculated for the conversion of FFA. Ferric sulfate was used to catalyze the esterification of short chain organic acid with alcohol, and showed a good activity as a solid Lewis acid [17,18]. The results in this study showed that the methanolysis of FFA in the WCO can be also divided into three phases (Fig. 5), and it is quite similar to the acid catalyzed process. In the first phase, over 85% of FFA was converted into FAME with 0.5 h; the excess of boiling methanol was easy to react with FFA. In the second one, the rate of methanolysis was slowed down from 0.5 to 2 h; but the conversion of FFA into FAME was over 95%. In the third one, the reaction of methanolysis approved to equilibrium after 2 h, prolonging the reaction time did not efficiently increase conversion of FFA.

3.2.1.2. Effect of amount of ferric sulfate on FFA conversion.

Fig. 6 shows the effect of the amount of ferric sulfate on FFA conversion. The conversion of FFA was quite slow without catalyst. In a low concentration (<1%) of catalyst, the conversion of FFA increased rapidly with the increasing amount of catalyst. When 1% of ferric sulfate was added, 94.4% of FFA was converted into FAME in 3 h. However, when the amount of catalyst exceeded 2%, the rate of reaction increased little.

3.2.2. Effect of mole ratio of methanol to TG on FFA conversion

The excess of methanol is necessary for the esterification of FFA with methanol because it can increase the rate of methanolysis. Normally, mole ratio of methanol to TG is near 6:1 when the alkali-catalyzed process is used. However, it increases to 30:1 even 50:1 in the acid catalyzed one to ensure the conversion [12].

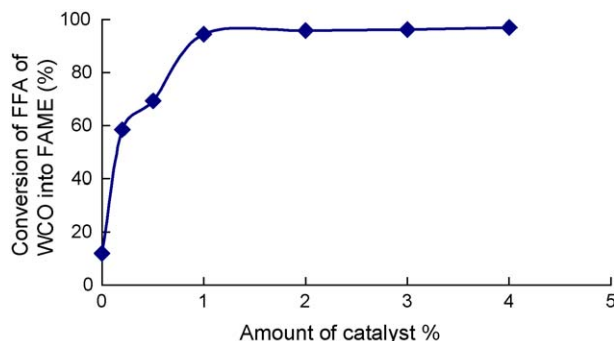


Fig. 6. Effect of amount of catalyst (ferric sulfate) on the conversion of FFA of WCO into FAME. Reaction temperature 95 °C, reaction time 3 h, and methanol to TG in mole ratio 10:1. FFA, free fatty acid; WCO, waste cooking oil; FAME, fatty acid methyl ester.

The conversion of FFA achieved 91.6% in 3 h when the ratio of methanol to TG was 3:1 (Fig. 7). The more excess of methanol was added, the higher conversion of FFA to FAME was achieved in the same reaction time. However, when the ratio was over 7:1, the increment of conversion was low.

3.2.3. Recovery of catalyst

After methanol recovery, the ferric sulfate was settled in the down layer of the reaction system. Because of absorption of some producing water and oil from the upper layer, the impurities in the ferric sulfate must be removed before the catalyst reused. Ashing is an easy way to get rid of these organic matters. After 5 h ashed under 460 °C, the recovered ferric sulfate was collected as the catalyst for the methanolysis of FFA and methanol. The compared results of the AVs of the oil layer of both recovered catalyst and fresh one showed that it was no significant difference of catalyzed efficiency between these two types of catalyst. Both AVs of the oil layer after methanol recovery of the recovered and fresh ferric sulfate catalyzed were approximately 2.2 mgKOH/g with the reaction time of 4 h, ratio of methanol to TG 10:1, and reaction temperature 95 °C. The reason why the recovered catalyst has high activity is that the organic impurities are completely removed by the ashing and the ferric sulfate is quite stable. However, due to the some solubility in methanol but low in the oil, the very fine ferric sulfate formed after methanol evaporation was suspended in the oil. Only 90% of whole amount catalyst was recovered when 2% of catalyst

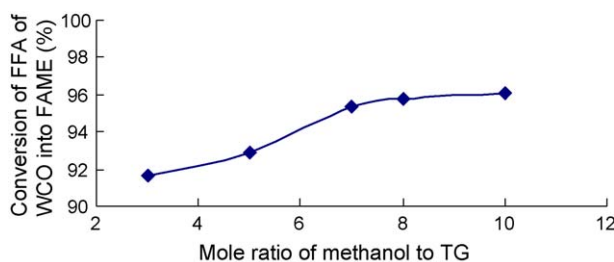


Fig. 7. Effect of methanol to TG in mole ratio on the conversion of FFA of WCO into FAME. Reaction temperature 95 °C, reaction time 3 h, and amount of ferric sulfate 3% (w/w, WCO). FFA, free fatty acid; WCO, waste cooking oil; FAME, fatty acid methyl ester.

was used at each performance at the optimal condition, indicating that the ferric sulfate may be reused for 10 times with 10% of fresh addition.

3.2.4. Alkali catalyzed transesterification of WCO

The parameter of alkali catalyzed transesterification of WCO that was pretreated by the ferric sulfate catalysis was selected from the reference. After 1 h of reaction, the mixture was left to settle to separate into two layers after methanol recovery. The dried upper layer analyzed by GC showed that the purity of biodiesel (FAME) was 97.02%. The base-catalyzed transesterification was very sensitive to the purity of the reactant. When the FFA content was over 0.5% in the oil, the efficiency of reaction would be held back in some extent [12]. In fact, the alkali catalyzed transesterification of used cooking oil could work even the FFA content was over 1% [19]. In this work, although the lowest AV of the WCO pretreated by the ferric sulfate was 2.10 ± 0.04 mgKOH/g, the transesterification of TG with methanol was easy to perform. The soap caused by the reaction of potassium hydroxide and FFA would not hinder the reaction of transesterification for the amount was little and viscosity of system was low. The soapstock was obtained by the washing of the crude biodiesel with hot water, and was removed by the centrifugation.

3.2.5. Distillation of FAME

The FAME (biodiesel) is easier to distillate than the FFA since the boiling point was relatively lower. The first distillate of the biodiesel was collected at 180 °C under vacuum (40 ± 5 mmHg). The distillation was terminated when no more FAME came out at the temperature 240 °C (40 ± 5 mmHg), 93.0% of the biodiesel obtained. Because distillation of the biodiesel in this study was a batch process, the double bond of unsaturated FAME would be dimerized as the residue of the distillation under high temperature (≥ 200 °C) and long time (≥ 0.5 h). Distillation of biodiesel under the lower vacuum to decrease the distillation temperature or by a wipe film evaporator with continuous distillation should minimize the dimerization of the unsaturated FAME and improve the output.

Distillation is the final purification step for the biodiesel produced by the WCO. In some countries of the EU where the biodiesel is used as a fuel without blended with fossil fuel, the crude biodiesel should be distilled as the final product before used. When the high acid value oil such as the WCO and the rice bran oil are used as the reactant, it is common to introduce the distillation for the final purification of biodiesel to remove the impurities and the unpleasant odor [12,21]. Theoretically, there is no residual iron in the final product after alkali catalysis and distillation due to the much higher boiling point of ferric sulfate than FAME. So, as the catalyst, ferric sulfate does not affect the oxidative stability of the final refined biodiesel.

4. Conclusion

1. The WCO can be converted into biodiesel directly by one-step sulfur acid catalyze process. The conversion of WCO was $\geq 90\%$, at the reaction time of 10 h and mole ratio of

methanol to TG 20:1. The disadvantages with this process are acidic effluent, no reusable catalyst and high cost of equipment.

2. Ferric sulfate acted as heterogeneous acid catalyst shows good activity to catalyze the methanolysis of FFA in the WCO. Compared with sulfur acid, this catalyst is environmental friendly, easy to be separated from the system, more efficient, reusable, and does not demand for high cost equipment for anti-corrosion.
3. The conversion of FFA in the WCO reached 97.22% at the reaction time of 4 h, catalyst of 2%, mole ratio of methanol to TG of 10:1, and reaction temperature of 95 °C.
4. This two-step catalyzed process provides a simple and economic method to produce biodiesel from the WCO. The byproducts of glycerol and soapstock in this process can be easily handled compared with the acid catalyzed one.

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