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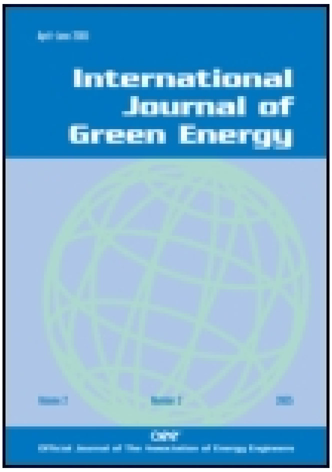

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The Completion of Esterification of Free Fatty Acids in Zanthoxylum Bungeanum Seed Oil with Ethanol

Junhua Zhang [a], Chengsen Cui [a], Haidong Chen [a] & Jianjun Liu [a]
[a] College of Forestry, Northwest A&F University, Yangling, China

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THE COMPLETION OF ESTERIFICATION OF FREE FATTY ACIDS IN *ZANTHOXYLUM BUNGEANUM* SEED OIL WITH ETHANOL

Junhua Zhang, Chengsen Cui, Haidong Chen, and Jianjun Liu
College of Forestry, Northwest A&F University, Yangling, China

In this work, the esterification of free fatty acids (FFA) in Zanthoxylum bungeanum seed oil (ZSO) with ethanol was performed and the effects of ethanol-to-oil molar ratio (8:1–32:1), catalyst amount (0.3–3.5% wt. of oil), reaction temperature (30–65°C), and reaction time (20–180 min) on the esterification of FFA were investigated. The acid value could not be reduced from beyond 40 mg KOH/g to less than 2 mg KOH/g by two-step sulfuric acid-catalyzed esterification with ethanol. Our results revealed that water formation during esterification was not a crucial factor inhibiting the completion of esterification. A novel technique to reduce acid value from above 40 mg KOH/g to less than 2 mg KOH/g was developed by using a second-step esterification with methanol. During the second-step esterification with methanol, some fatty acid ethyl esters were transformed into fatty acid methyl esters, which was confirmed by ^1H NMR.

Keywords: ***Esterification; Free fatty acids; Biodiesel; Ethanol; Methanol***

INTRODUCTION

The most commonly used method to produce biodiesel is transesterification of vegetable oils and animal fats with alcohols, and the reaction can be catalyzed by alkalis, acids, or enzymes (Ma and Hanna 1999; Demirbas 2007; Balat 2008). Alkali-catalyzed transesterification is much faster than acid-catalyzed or enzyme-catalyzed transesterification and is most commonly used commercially.

Currently, the cost of biodiesel cannot compete with petroleum-derived diesel mainly due to its relatively high cost of feedstocks. Thus, the use of inexpensive and non-edible fats and oils is an alternative substitute (Zhang et al. 2003; Veljković et al. 2006; Puhan et al. 2007; Kabir et al. 2009). Unfortunately, many cheap and non-edible feedstocks contain high amount of free fatty acids (FFA), which will react with alkaline catalysts to produce soap and inhibit the transesterification for biodiesel production (Van Gerpen et al. 2004). Therefore, FFA in feedstocks must be removed before alkali-catalyzed transesterification. A two-step process combining acid-catalyzed esterification followed by alkali-catalyzed transesterificaion has been recommended by many authors (Canakci and Van Gerpen 2001; Ramadhas, Jayaraj, and Muraleedharan 2005; Berchmans and Hiata 2008; Kafuku and Mbarawa 2010). According to the suggestion of several researchers, the acid values of

Address correspondence to Junhua Zhang, College of Forestry, Northwest A&F University, 3 Taicheng Road, Yangling 712100, Shaanxi Province, China . E-mail: junhuazhang@nwsuaf.edu.cn

feedstocks used for alkali-catalyzed transesterification should be less than 2 mg KOH/g, corresponding to a FFA content of 1% (Freedman, Pryde, and Mounts 1984; Mittelbach, Pokits, and Silberholz 1992; Satyanarayana and Muraleedharan 2010). Relatively low conversion was obtained in alkali-catalyzed transesterification from vegetable oils containing high FFA content (Burton, Fan, and Austic 2010; Bojan, Chelladurai, and Durairaj 2011).

Many studies have been carried out on biodiesel production using different alcohols, such as methanol, ethanol, propanol, isopropanol, butanol, or the mixture of methanol and ethanol (Ma and Hanna 1999; Warabi, Kusdiana, and Saka 2004; Demirbas 2007; Marchetti, Miguel, and Errazu 2007a, 2007b; Joshi et al. 2009). Although methanol is the most common alcohol used in transesterification process due to its low cost, in the case of methanolysis, the solubility of oil in methanol is less and the transesterification is mass transfer limited. Nowadays, there is a growing interest in the application of ethanol for biodiesel production since it is safe to handle and can be produced from renewable resources, thereby reducing the dependency on petroleum sources. Furthermore, ethanol has better solvent properties, possesses higher solubility for oils, and reduces the mass transfer limitation (Issariyakul et al. 2007). Oleic acid was esterified with ethanol using $SnCl_2$ and the yield of esterification increased steadily to a maximum value of about 90% with ethanol-to-oil molar ratio 120:1, catalyst amount 26.9%, reaction temperature 78°C, and reaction time 2 h (Cardoso, Neves, and da Silva 2009). The esterification of FFA in model-refined sunflower oil was carried out with ethanol and the amount of FFA was reduced from 21.4 mg KOH/g to 1.1 mg KOH/g (Marchetti and Errazu 2008). Some non-edible feedstocks have a high amount of FFA up to 25% (corresponding to an acid value of 50 mg KOH/g) and the acid values of those feedstocks should be reduced to a low level (less than 2 mg KOH/g) before alkali-catalyzed transesterification.

In the present work, the variables affecting the esterification of FFA in *Zanthoxylum bungeanum* seed oil (ZSO) with ethanol were investigated. A second-step acid-catalyzed esterification of FFA in ZSO with ethanol or methanol was conducted, which was monitored by ^{1}H NMR. This work aims to develop a method to reduce the FFA content in ZSO to a low level by acid-catalyzed esterification with ethanol.

MATERIALS AND METHODS

Materials

Ethanol anhydrous, methanol anhydrous, sulfuric acid (98%), oleic acid, anhydrous sodium sulfate, and other chemicals were of analytical reagent grade. ZSO was provided by a local company located in Hancheng, Shaanxi Province, China. The ZSO was obtained after *Zanthoxylum bungeanum* seed was collected and stored at room temperature for several months. The fatty acid composition of ZSO was as follows: oleic acid 34.88%, linoleic acid 25.72%, linolenic acid 17.12%, palmitic acid 11.45%, palmitoleic acid 9.72%, and stearic acid 1.11%. Its initial acid value was 17.0 mg KOH/g, corresponding to an FFA level of 8.5%. In order to investigate the effect of ethanol on the esterification of ZSO with different content of FFA, simulated ZSO with different degree of FFA were prepared by adding oleic acid to ZSO. After oleic acid addition, the acid values of ZSO increased to 40.1 and 74.2 mg KOH/g, respectively. Oleic acid was chosen because it is one of the dominant fatty acids in ZSO.

Esterification of ZSO with Ethanol

The reaction was carried out in a round-bottomed flask equipped with a reflux condenser and placed in a water bath with a temperature controller. The oil fed into the flask was preheated before the catalyst and alcohol was added. Sulfuric acid dissolved in ethanol was also preheated and added to the flask. The mixture was stirred at the same speed of 600 rpm for all test runs. After the reaction, the mixture was allowed to settle in a separating funnel overnight and the top ethanol–water layer was removed. The bottom layer was moved to a rotational evaporator to recover residual alcohol under vacuum at 65°C. After that, the bottom layer was washed at least four times using hot water (80°C) and dried with enough anhydrous sodium sulfate. The remaining product was used for acid value determination. In our experiments, two replications were carried out and the average values were presented.

The variables affecting the sulfuric acid-catalyzed esterification of ZSO with different levels of FFA, such as ethanol-to-oil molar ratio (8:1–32:1), catalyst amount (0.3–3.5% wt. of oil), reaction temperature (30–65°C), and reaction time (20–180 min) were studied by using conventional one-factor-at-a-time method. Based on pretest of esterification with ethanol, the general conditions used are ethanol-to-oil molar ratio 24:1, catalyst amount 2%, temperature 60°C, and reaction time 80 min.

The Second Step Esterification of ZSO

Ethanol or methanol was used for further esterification of residual FFA in ZSO. The reaction was performed in the same system as mentioned earlier. Sulfuric acid was also used as a catalyst. After the reaction, the oil was purified, washed, and dried as described previously.

Analysis

The acid value was determined according to the National Standard of China (1998). Two grams of sample was added into a 250 ml flask, after that 100 ml ether/ethanol (2:1, v/v) solution using a solvent was added. Three drops of phenolphthalein as an indicator was added to the solution. Titration was conducted using 0.1 M potassium hydroxide solution. The acid value was calculated in accordance with the following equation:

$$\mathrm{AV} = \frac{v \times N \times 56.1}{W}$$

where AV is the acid value (mg KOH/g), v is the consumption of 0.1 M KOH (ml), N is the true concentration of KOH (mol/l), and W is the weight of the sample (g).

^{1}H NMR analyses were performed on a Varian INOVA-400 MHz spectrometer (Varian, USA) using $CDCl_3$ as the solvent, and tetramethylsilane as the internal standard. In order to monitor the formation of ethyl ester in esterification of FFA with ethanol, the peak areas of $A1/A2$ in the region of 4.05–4.40 ppm in ^{1}H NMR spectra was calculated, in which the term A_1 corresponds to the area related to glycerol hydrogen atoms and A_2 corresponds to the area of the ethoxy quartet of ethyl esters with glycerol peaks (Neto et al. 2004).

RESULTS AND DISCUSSION

Esterification of FFA with Ethanol

Effect of ethanol-to-oil molar ratio. During acid-catalyzed esterification with alcohol, FFA is converted to biodiesel and a byproduct, water. Water formation is the major handicap of the completion of acid-catalyzed esterification of FFA (Canakci and Van Gerpen 1999). In addition, the reaction is reversible and alcohol should be in excess so as to drive the equilibrium toward products. The molar ratio of alcohol-to-oil has been reported to be one of the most important variables affecting the conversion of FFA (Ghadge and Raheman 2005; Veljković et al. 2006; Farag, El-Maghraby, and Taha 2011). To investigate the influence of ethanol-to-oil molar ratio on the reduction of the acid value of ZSO, six different ethanol-to-oil molar ratios in the range of 8:1–32:1 were investigated (Figure 1). With an 8:1 ethanol-to-oil molar ratio, the acid values of ZSO decreased from 17.0, 40.1, and 74.2 mg KOH/g to 3.9, 6.6, and 14.5 mg KOH/g respectively. With further increase in the ethanol-to-oil molar ratio, there was little improvement in the reduction of acid value of ZSO sample with an acid value of 17.0 or 40.1 mg KOH/g. For the ZSO with an initial acid value of 74.2 mg KOH/g, the acid value was achieved to 5.1 mg KOH/g when the ethanol-to-oil molar ratio increased to 20:1. There was not much effect on reducing the acid value with further increasing of the ethanol-to-oil molar ratio. When the ethanol-to-oil molar ratio was 32:1, the acid values of these three samples were decreased to 1.9, 2.3, and 4.4 mg KOH/g, respectively. As described earlier, water formation is a crucial problem during esterification due to its inhibition to the completion of esterification. One approach is to add excess alcohol, by which the water produced in esterification will be diluted to a low level. Somewhat surprisingly, the acid value did not decrease from beyond 40 mg KOH/g to a low level less than 2 mg KOH/g with a 32:1 ethanol-to-oil molar ratio. When methanol was used for sulfuric acid-catalyzed esterification, the ZSO having an acid value above 45 mg KOH/g was reduced to 1.9 mg KOH/g with a 16:1 methanol-to-oil molar ratio (Zhang and Jiang 2008). Our results indicated that the lower conversion of FFA was

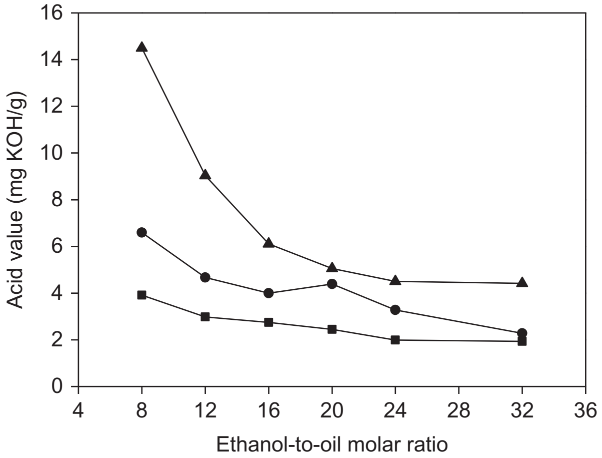

Figure 1 Effect of ethanol-to-oil molar ratio on reduction of acid value of different ZSO samples. ■: initial acid value 17.0 mg KOH/g; ●: initial acid value 40.1 mg KOH/g;▲: initial acid value 74.2 mg KOH/g (H_2SO_4 2%, reaction temperature 60°C, reaction time 80 min, rate of stirring 600 rpm).

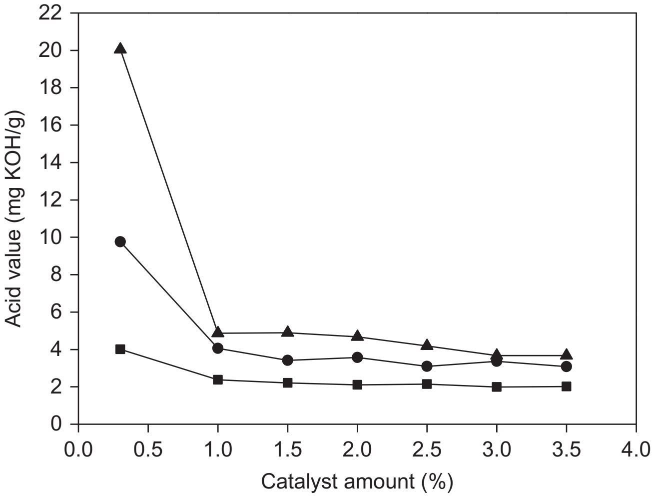

Figure 2 Effect of catalyst amount on reduction of acid value of different ZSO samples. ■: initial acid value 17.0 mg KOH/g; ●: initial acid value 40.1 mg KOH/g;▲: initial acid value 74.2 mg KOH/g (ethanol-to-oil molar ratio 24:1, temperature 60°C, reaction time 80 min, rate of stirring 600 rpm).

normally obtained in esterification with ethanol compared with methanol, and the acid value of ZSO did not decrease to less than 2 mg KOH/g by one-step esterification under the tested conditions.

Effect of catalyst amount. The effect of catalyst amount varied in the range of 0.3%–3.5% for seven different values that were investigated and the results are shown in Figure 2. The acid values of ZSO decreased from 17.0, 40.1, and 74.2 mg KOH/g to 4.0, 9.8, and 20.0 mg KOH/g, respectively, with the presence of a catalyst amount of 0.3%. When the catalyst amount increased to 1.0%, the acid values of three ZSO samples were all reduced to less than 5 mg KOH/g. It was also observed that increasing catalyst amount beyond 1.0% did not have clear effect on reducing the acid values of ZSO.

Effect of reaction temperature. The reaction was carried out at constant ethanol-to-oil molar ratio of 24:1, catalyst amount of 2%, and reaction time of 80 min. Figure 3 shows the variations of the reaction temperature for different feedstocks. It can be seen that ZSO with a high acid value of 74.2 mg KOH/g can be reduced to less than 8 mg KOH/g at a reaction temperature of 30°C. With further increase in reaction temperature, there was little improvement in the reduction of acid value of ZSO. For ZSO with an acid value beyond 40 mg KOH/g, the acid value could not be decreased to less than 2 mg KOH/g at the reaction temperatures varying from 30°C to 65°C.

Effect of reaction time. The effect of reaction time on the reduction of the acid value of ZSO was investigated with ethanol-to-oil molar ratio of 24:1, catalyst amount of 2%, and reaction temperature of 50°C (Figure 4). In the first 20 min, the esterification had a high reaction rate and the acid values of ZSO with different initial FFA contents decreased to less than 6 mg KOH/g. It was noticeable that the acid value of ZSO with initial acid value above 40 mg KOH/g could not decrease to less than 2 mg KOH/g by extending the reaction time to 180 min.

Our results presented here indicated that the ZSO with an initial acid value higher than 40 mg KOH/g could not be reduced to less than 2 mg KOH/g by one-step sulfuric

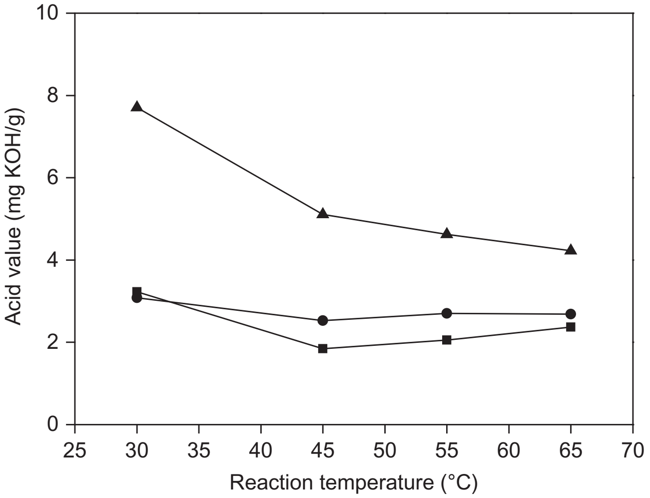

Figure 3 Effect of reaction temperature on reduction of acid value of different ZSO samples. ■: initial acid value 17.0 mg KOH/g; •: initial acid value 40.1 mg KOH/g;▲: initial acid value 74.2 mg KOH/g (ethanol-to-oil ratio 24:1, H_2SO_4 2%, reaction time 80 min, rate of stirring 600 rpm).

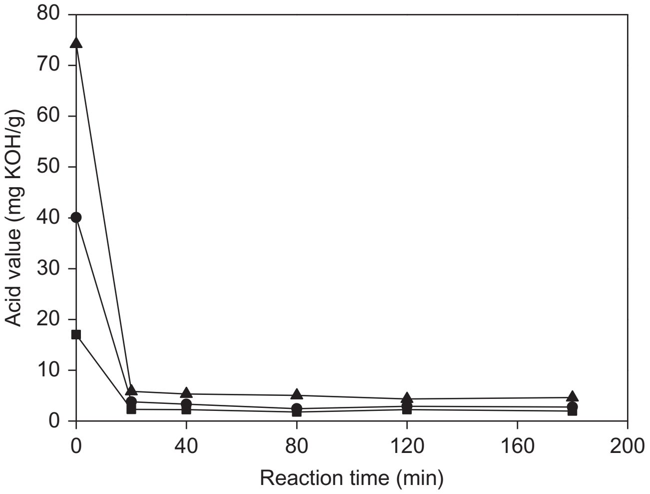

Figure 4 Effect of reaction time on reduction of acid value of different ZSO samples. ■: initial acid value 17.0 mg KOH/g; •: initial acid value 40.1 mg KOH/g;▲: initial acid value 74.2 mg KOH/g (ethanol-to-oil ratio 24:1, H_2SO_4 2%, temperature 50°C, rate of stirring 600 rpm).

acid-catalyzed esterification with ethanol under the tested conditions. The hypothesized reason is that water formation is sensitive to the esterification with ethanol, thereby inhibiting the completion of esterification.

Influence of Water on Esterification

In order to eliminate the influence of water formation on esterification, the ZSO after the first-step esterification with ethanol was separated and water was removed from the oil

Table 1 The Second Step Esterification of Different Pretreated ZSO with Ethanol. ZSO was Pretreated by Esterification with Ethanol using Sulfuric Acid as a Catalyst (Catalyst Amount 2%, Reaction Temperature 60°C, Reaction Time 60 min)

Initial acid value (mg KOH/g)	Ethanol-to-oil molar ratio	Final acid value (mg KOH/g)
7.03	6 : 1	4.50
5.23	6 : 1	2.90
7.24	12 : 1	3.42
5.23	12 : 1	2.97

with enough anhydrous sodium sulfate. A second-step esterification of ZSO with ethanol or methanol was carried out.

Our results revealed that the acid values of ZSO with an initial acid value that varied from 5.2 to 7.2 mg KOH/g could not go below 2 mg KOH/g even with12:1 ethanol-to-oil molar ratio, catalyst amount 2%, reaction temperature 60°C, and reaction time 60 min (Table 1). Obviously, water formation was not the key factor for the limitation of the esterification of FFA with ethanol. To the best of our knowledge, however, there was no report about the problem that the acid value of vegetable oil having high FFA content (beyond 40 mg KOH/g) could not be reduced to less than 2 mg KOH/g by two-step acid-catalyzed esterification with ethanol.

Somewhat surprisingly, when methanol was used as alcohol in the second-step esterification, the acid values of ZSO with an initial acid value that varied from 2.4 to 8.3 mg KOH/g reached 1.5 mg KOH/g. Such difference between ethanol and methanol in the second-step esterification may be caused by the relatively lower reaction activity of ethanol in the esterification of FFA, and which limited the reaction when the amount of FFA was low.

Monitoring Esterification with Ethanol and Methanol by ^{1}H NMR

After the acid value of ZSO was reduced to 5.6 mg KOH/g, the ratio of A_1/A_2 of ZSO and the pretreated ZSO was reduced from 0.60 to 0.42 (Figures 5a and b), which indicated the formation of ethyl esters after esterification of FFA in ZSO with ethanol. In the ^{1}H NMR spectra of methyl esters, signals at approximately 3.7 ppm are relate to protons of methyl ester (Gelbard et al. 1995; Knothe 2000). There was no methyl ester-related signal (at about 3.7 ppm) observed in the spectrum of ZSO after the first-step esterification with ethanol (Figure 5(b)). The FFA in the first-step pretreated ZSO was further esterified with methanol and the final acid value achieved to less than 2 mg KOH/g. The signal at 3.66 ppm was assigned to the protons of the methyl ester, which supported that FFA in the pretreated ZSO was transformed into methyl ester during the second-step esterification with methanol (Figure 5c). It was observed that the ratio of A_1/A_2 of ZSO after the second-step esterification was 0.48, which was higher than that of the pretreated ZSO (0.42). Our results indicated that some fatty acid ethyl esters were hydrolyzed and the FFA formed was transformed into fatty acid methyl esters during the second-step esterification with methanol. It may be caused by the hydrolysis of some fatty acid ethyl esters and the released FFA were consequently esterificated with methanol.

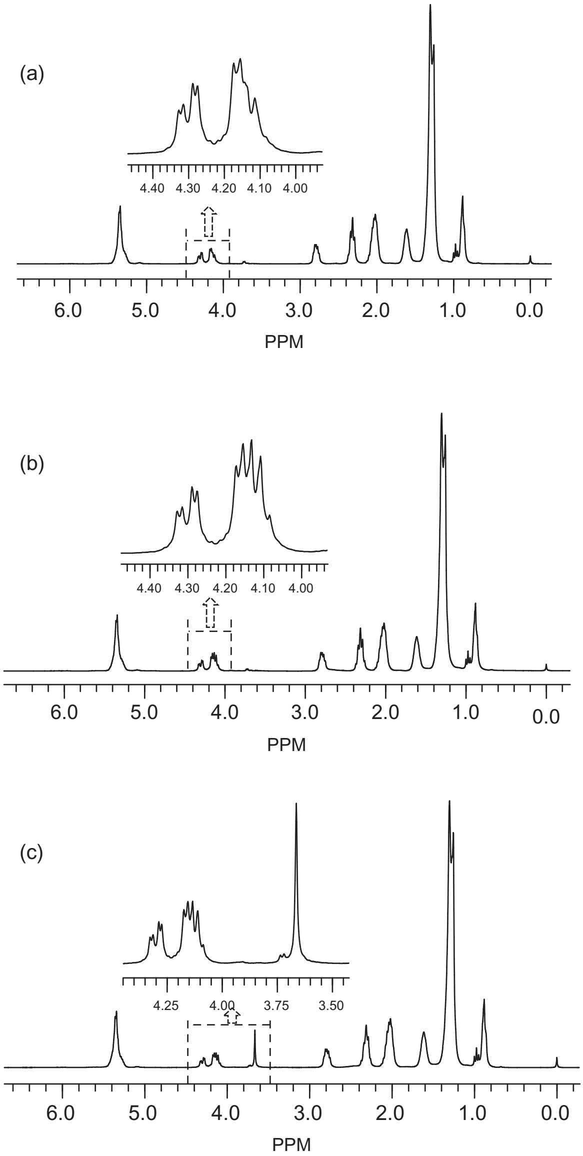

Figure 5 ^{1}H NMR spectra of ZSO before esterification (a), ZSO after the first-step esterification with ethanol (b), and ZSO after two-step esterification with ethanol followed by methanol (c).

Completion of Esterification with Ethanol and Its Application

Previously, in the esterification of FFA in ZSO with ethanol, the results presented here indicated it was difficult to complete the esterification using ethanol as alcohol. In the second-step esterification, methanol showed higher reaction activity than ethanol in the esterification of FFA and much lower acid value was observed (less than 2 mg KOH/g). By the method using two-step acid-catalyzed esterification followed by alkali-catalyzed transesterification, higher amounts of alcohol and catalysts would be necessary but all these reactions would be completed in a short time at low temperature. Acid-catalyzed transesterification, despite its insensitivity to FFA in the feedstock, has been largely ignored mainly because of its relatively slower reaction rate and higher reaction temperature (Zhang et al. 2003).

The novel technique developed here can be used for biodiesel production from high FFA-containing vegetable oils and ethanol. When other alcohols, such as propanol, iso-propanol, or butanol, was used in esterification of FFA in vegetable oils, a second-step esterification with methanol showed great potential application to complete the esterification, and consequently the vegetable oil can be used for alkali-catalyzed transesterification, which is the most commonly used method for biodiesel production.

CONCLUSIONS

The variables, ethanol-to-oil molar ratio and catalyst amount, were found to clearly influence the efficiency of esterification with ethanol using sulfuric acid as a catalyst. The esterification rate was very fast in the first 20 min. The high amount of FFA (beyond 40 mg KOH/g) could not be reduced to a low level (2 mg KOH/g) by two-step sulfuric acid-catalyzed esterification with ethanol, which indicated that water formation was not a crucial factor inhibiting the completion of the esterification with ethanol. In the second-step esterification, the reaction was almost completed when methanol was used as alcohol indicating its higher reaction activity than ethanol. Such a novel technique developed can reduce high-content FFA in vegetable oil to less than 1%.

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