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Lewis acid-catalyzed transesterification and esterification of high free fatty acid oil in subcritical methanol

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Abstract–Lewis acid catalysts are active for both esterification and transesterification, but the reaction is very slow due to mass-transfer limitations between methanol and oil phase. Because oil, FFA and Lewis acid catalysts are all soluble in the subcritical methanol phase, the esterification and transesterification will be enhanced when they are carried out under subcritical conditions. In this work, the esterification and transesterification of high FFA oil to biodiesel via Lewis acid catalysts such as $Pb(OOCCH_3)_2$, $Cd(OOCCH_3)_2$ and $Zn(OOCCH_3)_2$ were carried out in the subcritical methanol phase (2 MPa, 180 °C, reaction time 30 min). The results show that the esterification conversion reaches 79.8-96.4% with Palmitic acid as feedstock, and the transesterification conversion reaches 56.8-73.4% with soybean oil as feedstock. With the mixture of Soybean oil and Palmitic acid (FFA content of 20.3 wt%) as feedstock, the content of fatty acid methyl esters (FAME) in products reaches 67.3-83.4%.

Key words: Biodiesel, Subcritical Methanol, Lewis Acid Catalyst, Transesterification, Esterification

INTRODUCTION

Nowadays, most energy is derived from unrenewable fossil fuel, which has a great impact on environment, and there is an increasing demand for fuels. Hence the search for alternatives has gained much attention. For example, vegetable oils could be used as fuels in compression ignition engines. However, there are some problems because of high viscosity and low volatility in their direct use. The methods for solving these problems include blending with diesel, emulsification, pyrolysis, cracking [1] and transesterification. Biodiesel is the product of transesterification reaction and may play an important role in the future energy supply. Moreover, it has drawn much attention because of its environmental benefits. Generally, biodiesel can be produced by the transesterification of triglycerides with alcohols using an alkaline catalyst [2] or enzyme. In a conventional process, the refined or edible oils with the acid value being lower than 1 mgKOH/g are employed and the reaction system should be water-free; these result in high cost for the final products.

To reduce the production cost, less-expensive feedstock (raw or reclaimed) with high free fatty acid (FFA) should be used instead of refined oil. Hence a two-step process is generally necessary, i.e., fatty acid is converted to the methyl ester via acid-catalyzed esterification, while the conversion of glyceride is via alkaline catalyzed transesterification. The same problems exist in an enzyme-catalyzed process. By carrying out the transesterification in supercritical methanol, the use of catalyst can be avoided and the reaction becomes homogeneous, while the esterification of fatty acid can also be performed. However, the reaction conditions are very rigorous; this prevents it from successful commercialization [3-5].

Lewis acid catalysts were proved to be active for both esterification and transesterification reactions [6], but the reaction is very slow due to the limits of mass-transfer between methanol and oil phase in a conventional process. The esterification and transesterification will be enhanced under subcritical conditions, where oil, FFA and Lewis acid catalysts are all soluble in the subcritical methanol phase. Moreover, the reaction conditions remain much milder than that using supercritical methanol. Therefore, in this work, the esterification and transesterification of high FFA oil to biodiesel via Lewis acid catalysts such as $Pb(OOCCH_3)_2$, $Cd(OOCCH_3)_2$ and $Zn(OOCCH_3)_2$ were carried out in the subcritical methanol phase. The effects of reaction conditions and selection of catalysts on the production of fatty acid methyl esters (FAME) were then investigated.

EXPERIMENTAL

The reactions were performed in a 250 cm^3 autoclave at 120-200 °C. The reagents (soybean oil and palmitic acid) and catalyst (acetates of the Zn, Pb and Cd) were first introduced into the autoclave. When the autoclave was sealed and heated to the desired temperature at a fixed rate, the methanol was pumped into the autoclave until the system pressure reached 2 MPa. The reaction lasted for 30 min; after that the autoclave was cooled down and the reacting mixture was subjected to analysis.

The acid value of the product was determined by titration of KOH and the content of FAME was determined by a gas chromatograph (GC-14B) equipped with packed DEGS column and FID.

RESULTS AND DISCUSSION

1. Selection of Catalysts

The effects of various catalysts (lead acetate, cadmium acetate and zinc acetate) on the transesterification of soybean oil and esterification of Palmitic acid were examined, as shown in Table 1. The

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Table 1. Conversion of esterification and transesterification[a]

Feed	Catalyst	Conversion/%
Palmitic acid	$Pb(OOCCH_3)_2$	82.1
Palmitic acid	$Cd(OOCCH_3)_2$	79.8
Palmitic acid	$Zn(OOCCH_3)_2$	96.4
Soybean oil	$Pb(OOCCH_3)_2$	73.4
Soybean oil	$Cd(OOCCH_3)_2$	56.8
Soybean oil	$Zn(OOCCH_3)_2$	68.9

[a]Reaction conditions: 180 ml soybean oil or 160 g Palmitic acid as feed and 3 g catalyst was introduced; reaction lasted for 30 min at 180 °C and 2 MPa (through pumping methanol).

Table 2. Content of FAMEs in products for reaction with mixed feedstock[a]

Catalyst	Acid value (mgKOH/g)	Content of FAMEs (%)
$Pb(OOCCH_3)_2$	11.21	75.8
$Cd(OOCCH_3)_2$	16.64	71.5
$Zn(OOCCH_3)_2$	6.01	73.7

[a]Reaction conditions: 120 ml soybean oil+30 g Palmitic acid as mixed feed and 3 g catalyst was introduced; reaction lasted for 30 min at 180 °C and 2 MPa (through pumping methanol).

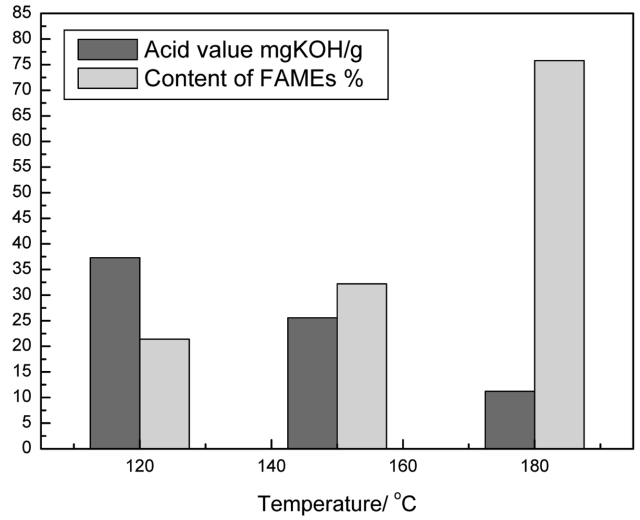

Fig. 1. Content of FAMEs in the product from reaction at different temperature[a].
[a]Reaction conditions: 120 ml soybean oil+30 g Palmitic acid as mixed feed and 3 g lead acetate as catalyst was introduced; reaction lasted for 30 min at 2 MPa (through pumping methanol).

esterification conversion reaches 79.8-96.4% with Palmitic acid as feedstock, and the transesterification conversion reaches 56.8-73.4% with soybean oil as feedstock. It showed that acetates are active in both esterification and transesterification reactions. For the esterification reaction, zinc acetate exhibits the highest catalytic activity, and the conversion of free fatty acid exceeds 95%; but for transesterification, lead acetate gives the highest catalytic activity.

For a mixed feedstock of 120 ml soybean oil and 30 g Palmitic acid, the results of esterification and transesterification are listed in Table 2. It is shown that a single step process is possible for both transesterification and esterification reactions in subcritical methanol. The catalyst lead acetate gives the highest content of FAMEs in the products, while with zinc acetate as catalyst the least acid value is obtained in product. The selection of catalyst may depend on the proportion of FFA in the feedstock.

2. Effects of Temperature on the Reaction Behaviors

Reaction temperature exhibited a significant influence on the esterification and transesterification results, as shown in Fig. 1. With lead acetate as catalyst, the content of FAMEs in the product is quite low at a temperature lower than 150 °C; at 180 °C; the content of FAMEs reaches 75.8% with the acid value of 11.21 (mgKOH/g).

3. Effects of Water on the Reaction Behaviors

To investigate the effects of water on the reaction behaviors, the esterification and transesterification were carried out with adding certain content of water in the feed (water/soybean oil=0, 0.045 and 0.14, respectively, by weight) at 180 °C and 2 MPa with lead acetate as catalyst. Water was generally thought to have strong depressive effects on the activity of acetates [6]. However, as listed in Fig. 2, water exhibited slight influence on the transesterification and esterification in the current study. The proper amount of water (water/soybean oil=0.045, by weight) in the feed may even be favorable for the reactions to FAMEs, because it could promote the hydrolysis of soybean oil and the esterification is some easier than the transesterification under the same conditions. However, an excess amount of water is thermodynamically unfavorable for the esterification.

4. Effects of Methanol Usage on the Reaction Behaviors

The molar ratio of methanol to soybean oil is an important factor for transesterification and esterification. It is well known that transesterification and esterification are reversible and the increase of methanol amount in the reaction system can shift the reaction equilibrium to yield FAMEs. The molar ratio of methanol to oil is about 30 during supercritical treatment [3-5].

As listed in Table 3, with the ratio of soybean oil to Palmitic acid

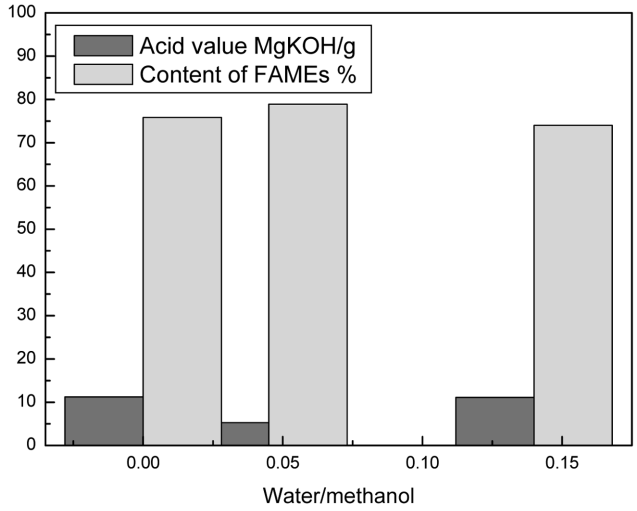

Fig. 2. Effects of water in the feed on the reaction results[a].
[a]Reaction conditions: 120 ml soybean oil+30 g Palmitic acid as mixed feed and 3 g lead acetate as catalyst was introduced; reaction lasted for 30 min at 180 °C and 2 MPa (through pumping methanol).

Table 3. Influence of methanol/oil molar ratio on the reaction results[a]

Feedstock	Acid value (mgKOH/g)	Content of FAMEs (%)
120 ml soybean oil+30 g Palmitic acid	25.58	32.2
40 ml soybean oil+10 g Palmitic acid	5.12	83.4

[a]Reaction conditions: lead acetate at amount of 2 wt% of feed was used as catalyst; reaction lasted for 30 min at 150 °C and 2 MPa (through pumping methanol).

(w/w) being 3.68 and at 150 °C, the conversion was very low with a low ratio of methanol to soybean oil. When the amounts of feed (soybean oil+Palmitic acid) decreased, i.e., with a high methanol/oil ratio, the transesterification and esterification are enhanced significantly.

CONCLUSIONS

The esterification and transesterification of high FFA oil to biodiesel via Lewis acid catalysts such as $Pb(OOCCH_3)_2$, $Cd(OOCCH_3)_2$ and $Zn(OOCCH_3)_2$ were carried out in the subcritical methanol phase. The results show that acetates are active for both transesterification and esterification in subcritical methanol, so a single step process is possible for production of biodiesel from oils with high FFA.

The esterification conversion reaches 79.8-96.4% with Palmitic acid as feedstock, and the transesterification conversion reaches 56.8-73.4% with soybean oil as feedstock at 180 °C and 2 MPa. With a mixture of Soybean oil and Palmitic acid (FFA content of 20.3 wt%) as feedstock, the content of fatty acid methyl esters (FAME) in products reaches 67.3-83.4%. Meanwhile, the reaction temperature and methanol/oil ratio exhibited a significant influence on the final results.

REFERENCES

1. W. Charusiri, W. Yongchareon and T. Vitidsant, *Korean J. Chem. Eng.*, **23**, 349 (2006).
2. Y. C. Bak, J. H. Choi, S. B. Kim and D. W. Kang, *Korean J. Chem. Eng.*, **13**, 242 (1996).
3. A. Demirbas, *Energy Conversion and Management*, **43**, 2349 (2002).
4. D. Kusdiana and S. Saka, *Bioresource Technology*, **91**, 289 (2004).
5. G. Madras, C. Kolluru and R. Kumar, *Fuel*, **83**, 2029 (2004).
6. M. Di Serio, R. Tesser, M. Dimiccoli, F. Cammarota, M. Nastasi and E. Santacesaria, *J. Mol. Catal. A: Chem.*, **239**, 111 (2005).