Biodiesel synthesis via homogeneous Lewis acid-catalyzed transesterification

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ABSTRACT

Lewis acids ($AlCl_3$ or $ZnCl_2$) were used to catalyze the transesterification of canola oil with methanol in the presence of terahydrofuran (THF) as co-solvent. The conversion of canola oil into fatty acid methyl esters was monitored by ^1H NMR. NMR analysis demonstrated that $AlCl_3$ catalyzes both the esterification of long chain fatty acid and the transesterification of vegetable oil with methanol suggesting that the catalyst is suitable for the preparation of biodiesel from vegetable oil containing high amounts of free fatty acids. Optimization by statistical analysis showed that the conversion of triglycerides into fatty acid methyl esters using $AlCl_3$ as catalyst was affected by reaction time, methanol to oil molar ratio, temperature and the presence of THF as co-solvent. The optimum conditions with $AlCl_3$ that achieved 98% conversion were 24:1 molar ratio at 110 °C and 18 h reaction time with THF as co-solvent. The presence of THF minimized the mass transfer problem normally encountered in heterogeneous systems. $ZnCl_2$ was far less effective as a catalyst compared to $AlCl_3$, which was attributed to its lesser acidity. Nevertheless, statistical analysis showed that the conversion with the use of $ZnCl_2$ differs only with reaction time but not with molar ratio.

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1. Introduction

Biodiesel is an alternative diesel fuel defined as the mono alkyl esters of long chain fatty acids derived from vegetable oils or animal fat. With the continuous uncertainty and increasing environmental impact associated with the utilization of petroleum-based diesel fuel, the demands for biodiesel had increased significantly in recent years. For instance, the global production of biodiesel had increased from about 0.5 billion litres in 1997–1.8 billion litres in 2003 [1]. The environmental, operational and economic benefits associated with the utilization of biodiesel as an alternative fuel for diesel engines have been demonstrated by numerous independent studies and have been well accepted [2–8].

While the base-catalyzed transesterification of vegetable oil or animal fat is the most adopted technology for biodiesel commercial production [3,9–10], the process makes the biodiesel of higher manufacturing cost compared to petroleum-based diesel fuel. The process is sensitive to the quality of the feedstock requiring vegetable oil or animal fat with very low amount of free fatty acid (FFA). The use of refined or high quality feedstock constitutes 80–88% of the overall production or manufacturing cost [3,5,11]. Efforts to find alternative vegetable oil for biodiesel production primarily with the aim of lowering the feedstock cost often suggested the utilization of waste cooking oil or non-edible vegetable oil containing high

amounts of FFA [12–14]. However, the high amounts of FFA in these oils make them unsuitable for base-catalyzed transesterification. High amounts of FFA resulted in extensive soap formation as FFA reacts with the catalyst, which is normally NaOH or KOH, via a saponification reaction. Soap renders biodiesel purification and catalyst removal even more challenging due to the formation of a stable emulsion generating a significant amount of waste water. The presence of high amounts of FFA in the feedstock therefore eventually leads to decreased biodiesel conversion and yield. In fact, studies have demonstrated that the amount of FFA in the feedstock for biodiesel production should not be higher than 0.5% in order to afford a product that passes the ASTM biodiesel standard [14].

Acid-catalyzed transesterification is more suitable for waste or unrefined oil. The process has not gained as much attention as the base-catalyzed transesterification because of the slower reaction rate and the very high methanol to oil molar ratio requirements. The two-step biodiesel process addressed this issue by using an acid catalyst followed by a normal base-catalyzed transesterification. The first step involved the esterification reaction between the methanol and FFA to produce the corresponding fatty acid methyl ester (FAME) using H_2SO_4, H_3PO_4 or recently, $Fe_2(SO_4)_3$ [12,15] as catalyst.

Several research efforts have also been performed on the use of Lewis or Bronsted acids as catalysts to convert vegetable oil into FAME in both homogeneous and heterogeneous systems. Heterogeneous Lewis acid catalyzed-transesterification was achieved using Fe–Zn double metal cyanide for the preparation of biodiesel

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and biolubricant from vegetable oil containing relatively high amount of FFA and water [16]. Sn, Pb and Zn complexes in the form M(3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$ have been demonstrated to be effective in homogeneous Lewis acid catalyzed-transesterification of vegetable oil via the formation of a four-membered ring transition state [17]. Another recent study used carboxylic salts of Cd, Mn, Pb and Zn as catalysts for biodiesel synthesis from vegetable oil containing high amount of free fatty acids [13].

This study presents the use of common Lewis acids, AlCl$_3$ and ZnCl$_2$, in biodiesel synthesis primarily to demonstrate an alternative catalyst for the simultaneous esterification of long chain fatty acid and transesterification of vegetable oil. Optimization of reaction conditions was performed and supported by statistical analysis.

2. Materials and methods

2.1. Transesterification of canola oil

Typical biodiesel preparation was performed by reacting 2.0 g of commercial canola oil with a known amount of methanol, THF and AlCl$_3$ or ZnCl$_2$ as catalyst at different reaction time and temperature. In all the runs, the amount of catalyst and THF were 5% (by weight based on oil) and 1:1 with respect to methanol (by weight), respectively. The reaction was conducted in a round bottom flask submerged in an oil bath attached to a reflux condenser, temperature controller and a magnetic stirrer. After the reaction, the excess methanol and THF were removed by vacuum distillation followed by extraction with petroleum ether or hexanes and filtration to remove the catalyst. The final product was obtained by removing the solvent by vacuum distillation.

2.2. Esterification of stearic acid

Stearic acid was transesterified following the procedure described above using AlCl$_3$ as catalyst at 110 °C with a molar ratio of methanol to stearic acid of 60 and a reaction time of 24 h.

2.3. Effect of THF

Since ZnCl$_2$ did not result in a satisfactory conversion, the effect of THF was investigated only with AlCl$_3$. The effect of THF was investigated using 5% AlCl$_3$ (by weight based on oil), 18 h reaction time with different values of methanol to oil molar ratio (6, 12, 24, 42 and 60). The transesterification was conducted following the procedure described above except that THF was not added in the system.

2.4. NMR analysis

All purified products were analyzed by ^{1}H NMR to determine the % conversion. About 30 mg of the sample was dissolved in CDCl$_3$ for the analysis. Spectra were recorded using a Bruker Avance 300 MHz NMR Spectrometer.

2.5. Statistical analysis

The effect of molar ratio and temperature on the conversion of canola oil to FAME were analyzed by univariate analysis of variance (ANOVA) to determine the optimum conditions for the reaction. Three different sets of experiments were tested individually: the use of AlCl$_3$ at 75 °C, AlCl$_3$ at 110 °C and ZnCl$_2$ at 110 °C.

3. Results and discussion

3.1. ^{1}H NMR analysis

The transesterification of canola oil with methanol using AlCl$_3$ or ZnCl$_2$ as catalyst was monitored by ^{1}H NMR. Fig. 1 shows the ^{1}H NMR spectra of canola oil and incompletely transesterified canola oil. The methylene glyceridic protons of the triglycerides resonated at around 4.3–4.5 ppm as two doublets while the glyceridic methine protons resonated at around 5.25 ppm (Fig. 1a) [18–20]. Percent conversion was calculated based on the integration values of the methylene glyceridic protons and methyl protons of the FAME, which resonated at 3.7 ppm (Fig. 1b). Note that the glyceridic protons of the intermediate products, mono- and diglycerides, also resonated at the same region as the methylene protons of the starting triglycerides. The glyceridic methine protons were not included in the calculation since the peak overlaps with the alkelinic protons of the unsaturated fatty acids of the triglycerides.

AlCl$_3$ was also used to esterify stearic acid with methanol. Fig. 2 shows the spectra of stearic acid and the purified product obtained from the esterification reaction. Again, the methyl protons of methyl stearate, which were absent in the ^{1}H NMR spectra of stearic acid, resonated at 3.7 ppm. The use of AlCl$_3$ to catalyze the esterification of stearic acid to methyl stearate resulted in 90% conversion. The catalyst therefore is suitable for simultaneous esterification of free fatty acid and transesterification of triglycerides. Using AlCl$_3$, the competing saponification reaction of free fatty acid could be eliminated giving higher FAME yield and purity even with the use of starting vegetable oil with high levels of free fatty acids.

3.2. Optimization of reaction conditions

3.2.1. AlCl$_3$ as catalyst: effect of reaction time, molar ratio and temperature

In a transesterification reaction of vegetable oil, three moles of methanol are required to react stoichiometrically for every mole of triglyceride molecule to give three moles of the corresponding FAME and a mole of glycerol. Since this reaction is reversible, methanol is usually added in excess of its stoichiometric amount to drive the reaction forward. In base catalyzed-transesterification, a molar ratio of 6 is enough to produce 96–98% conversion of vegetable oil with 0.5–1.0% (by weight based on oil) of catalyst for a 2 h reaction.

Acid catalyzed-transesterification of vegetable oil proceeds several times slower than its base catalyzed counterpart. This could be explained by the different mechanisms by which these two reactions occur. In base catalyzed-transesterification, a strong nucleophile methoxide ion is generated from the reaction of the base catalyst with methanol. The methoxide once produced easily attacks the carbonyl carbon to form a tetrahedral transition state that would eventually lead to the formation of the product. On the other hand in acid-catalyzed transesterification, the carbonyl group needs to be activated prior to the nucleophilic attack of methanol, which is a relatively weaker nucleophile. Hence, while it only takes about 2 h to afford 95–98% conversion of triglycerides to FAME under basic catalyst [21], acid catalyzed-transesterification normally requires 48 h reaction time to obtain a comparable conversion.

The variable parameters employed were reaction time (6, 18, 24 h), methanol to oil molar ratio (6, 12, 24, 42 and 60), reaction temperature (75, 110 °C), presence of THF as co-solvent (1:1 methanol to THF by weight in runs with THF), and type of catalyst (AlCl$_3$ or ZnCl$_2$). In all the runs, the catalyst amount was kept at 5% based on the weight of oil. For acid-catalyzed transesterification of waste cooking oil using H$_2$SO$_4$ as catalyst, Zheng and co-workers
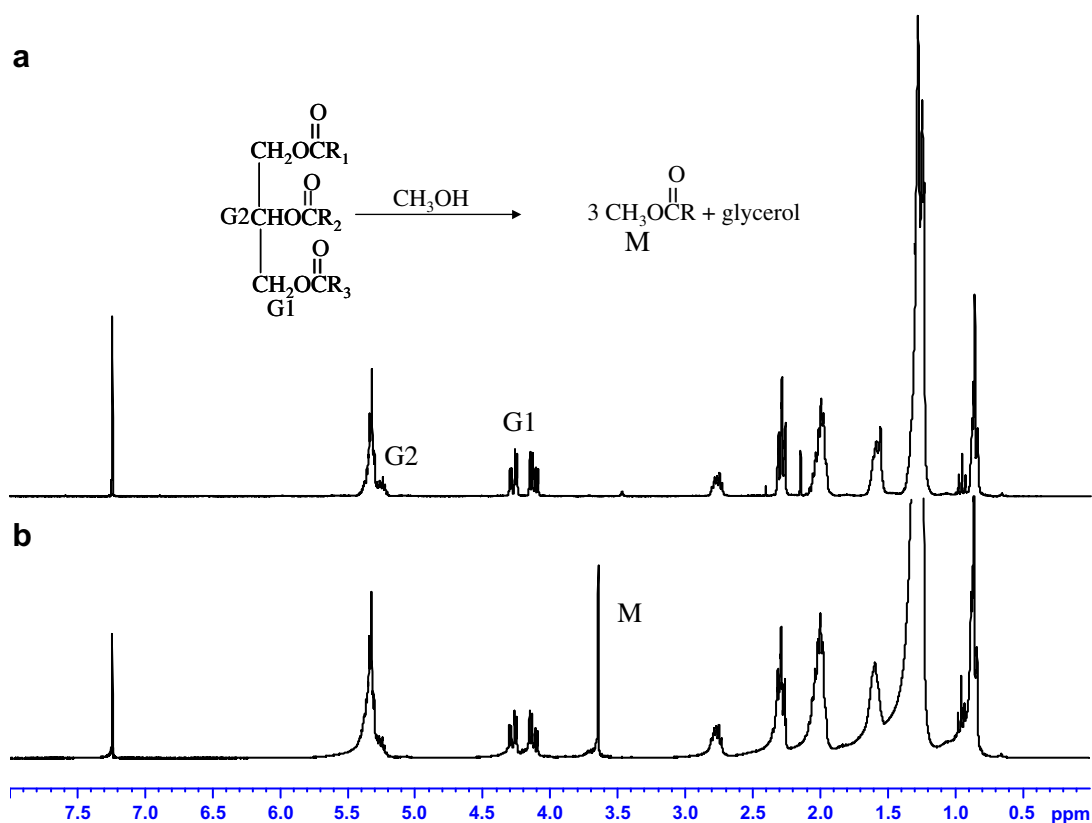
a

b

Fig. 1. ^1H NMR spectra of canola oil (a) and incompletely transesterified canola oil (b).

a

b
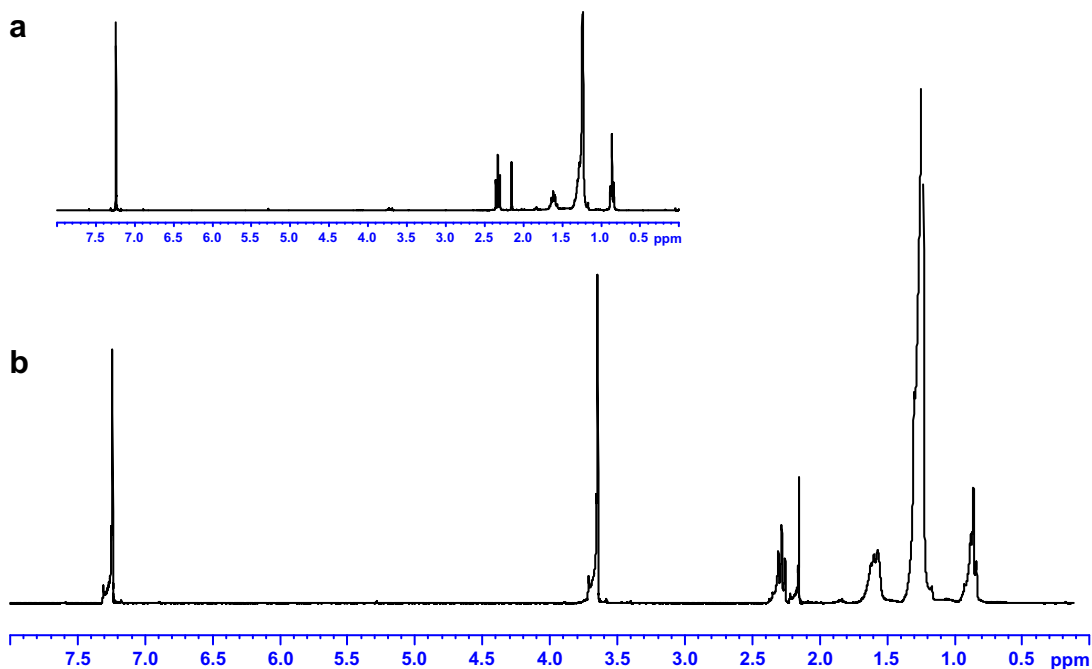
Fig. 2. ^1H NMR spectrum of stearic acid (a) and transesterified stearic acid (b) with 90% conversion.

[22] had identified that methanol:oil:catalyst molar ratios and reaction temperature were the most significant factors affecting the FAME yield. In the case of base-catalyzed transesterification, the yield and purity of the product is most affected by the initial concentration of the catalyst [23] and methanol to oil molar ratio [24].

The optimum conditions for the conversion of canola oil to FAME using $AlCl_3$ or $ZnCl_2$ were determined by univariate analysis of variance. Fig. 3 shows the effect of reaction time (Fig. 3a) and methanol to oil molar ratio (Fig. 3b) on the conversion of canola oil to FAME using $AlCl_3$ as catalyst at 75 °C. With methanol to oil

a

%conversion vs reaction time (hrs)

Factor:Time

Legend: 60, 42, 24, 12, 6

CONVERSION

		Subset	
TIME	N	1	2
Duncan[a,b] 6	5	26.7980	
18	4		61.6357
24	6		66.9878
Sig.		1.000	.570

Means for groups in homogeneous subsets are disp
Based on Type III Sum of Squares
The error term is Mean Square(Error) = 198.628.

a. Uses Harmonic Mean Sample Size = 4.865.

b. The group sizes are unequal. The harmonic me of the group sizes is used. Type I error levels a not guaranteed.

c. Alpha = .05.

b

%conversion vs molar ratio (MeOH to oil)

Factor: Molar ratio

Legend: 6, 18, 24

CONVERSION

		Subset	
MOLE RATIO	N	1	2
Duncan[a,b] 6	3	18.1275	
60	3		53.6149
12	3		59.6226
42	3		59.6549
24	3		69.7999
Sig.		1.000	.222

Means for groups in homogeneous subsets are display
Based on Type III Sum of Squares
The error term is Mean Square(Error) = 198.628.

a. Uses Harmonic Mean Sample Size = 3.000.

b. Alpha = .05.

Fig. 3. Effect of reaction time (a) and molar ratio (b) on the conversion of canola oil to FAME using 5% $AlCl_3$ as catalyst (by wt based on oil) at 75 °C and THF as co-solvent (1:1 methanol to THF by weight). In (a), different molar ratios were 6, 12, 24, 42, and 60. In (b), different reaction time were 6, 18, and 24 h. The tables show the results of statistical analysis using ANOVA.

molar ratio of 6, the reaction proceeds slowly affording only about 20% conversion after 24 h reaction. With molar ratios of 12 to 60, the reaction rates were almost the same from 6 to 18 h. At 95% confidence level, the % conversion at 6 h differs significantly from 18 and 24 h. Increasing reaction time from 18 to 24 h did not provide significant increase in the conversion.

At shorter reaction time (6 h), increasing the methanol to oil molar ratios did not result in a significant increase in the conversion giving only 40% maximum conversion even at higher molar ratios. On the other hand with 18 and 24 h reaction time, significant increases in the conversion were observed from 6 to 12 molar ratios and remain almost unchanged from 12 to 60 molar ratios. Statistical analysis showed that the conversion obtained from 6 molar ratio was significantly different from the conversion obtained from 12 to 60 molar ratios regardless of reaction time.

While the optimum conditions with the use of 5% $AlCl_3$ (based on weight of oil) was established at an 18 h reaction time and methanol to oil molar ratio of 24, the maximum conversion obtained was only in the range of 84–86%.

Since relatively lower conversions were obtained with the use of $AlCl_3$ at 75 °C, the transesterification at higher temperature was then conducted. Fig. 4 shows the effect of reaction time (Fig. 4a) and methanol to oil molar ratio (Fig. 4b) on the conversion of canola oil to FAME using $AlCl_3$ as catalyst at 110 °C as well as the results obtained from statistical analysis. The reaction time affects the conversion depending on the methanol to oil molar ratio. At lower molar ratio of 6, the conversion obtained from 6 to 18 h was only about 6–7% with a maximum conversion of 25% at 24 h reaction time. The rates of reaction from 6 to 24 h for molar ratios of 12–24, were similar and low. Under these conditions, the conversion ranges only from 81% to 98% suggesting that the commonly observed higher reaction rates at the beginning of transesterification reaction had occurred within the first 6 h of the reaction. The plot of % conversion vs reaction time with molar ratio of 42 and 60 was typical for transesterification. At 6 h reaction time,

the% conversion from higher molar ratios (42 and 60) was even lower than that obtained from lower molar ratios of 12 and 24.

The effect of methanol to oil molar ratio is clearly depicted in Fig. 4b. For both 75 and 110 °C, while the conversion had increased with increasing molar ratios from 6 to 12, further increase with molar ratio of 42 or 60 had decreased the conversion especially with 6 h reaction time. The presence of high excess of methanol could have deactivated the catalyst at this temperature. Another possibility for the decrease in conversion could be attributed to the recombination of FAME with glycerol considering that transesterification is a reversible reaction. In the presence of high amount of methanol, separation of glycerol and FAME into two layers is less favorable because of the higher solubility of glycerol in the system favoring the backward reaction [24]. Statistical analysis showed that the use of $AlCl_3$ at 110 °C has optimum conditions of 12–24 molar ratios conducted at 18 h reaction time to give a maximum conversion of 98%.

At any given reaction time and methanol to oil molar ratio, the conversion of canola oil to FAME had increased with increasing reaction temperature from 75 to 110 °C. While the optimum conversions at 75 and 110 °C differ by 12%, they were both obtainable with the use of a methanol to oil molar ratio of 24 and with reaction time of 18 h.

3.2.2. $ZnCl_2$ as catalyst: effect of reaction time and molar ratio

$ZnCl_2$ was less effective in catalyzing the transesterification of canola oil into FAME, which is attributed to its weaker acidity. Except with molar ratio of 60, increasing the reaction time did not result in a significant increase in the conversion, which ranged only from 3% to 22%. Nevertheless, statistical analysis showed that the conversions obtained from 6 and 18 h reaction times were not significantly different than the conversions from 18 and 24 h reaction times. Moreover, the absence of a plateau in Fig. 5a suggests that the conversion would still increase if the reactions were to extend more than 24 h. Statistical analysis also showed that the conversion does
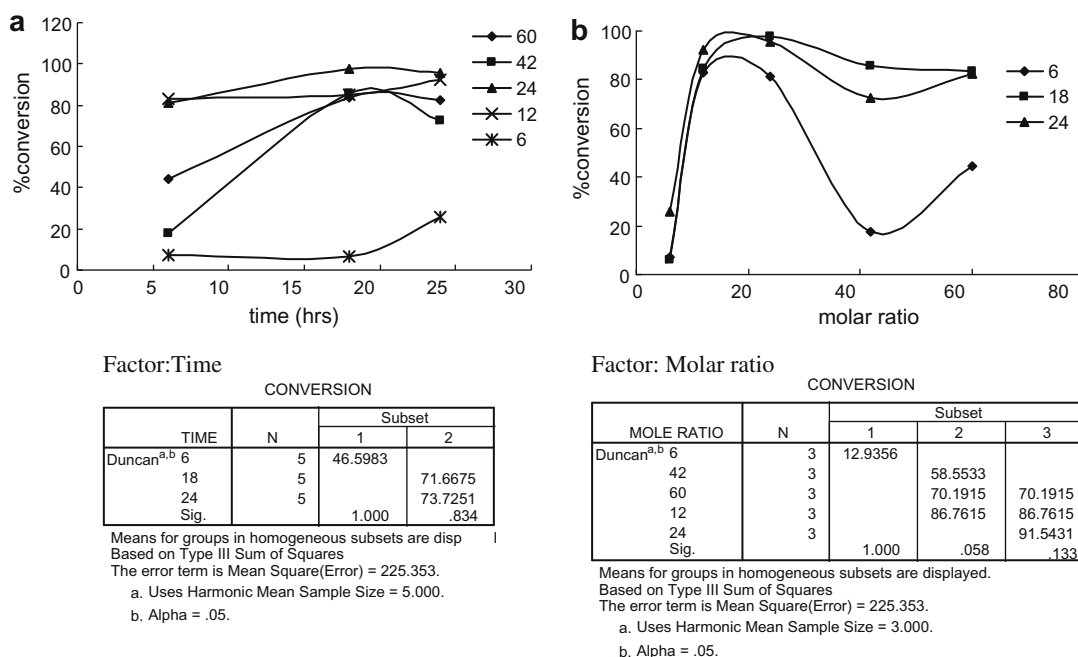
Fig. 4. Effect of reaction time (a) and molar ratio (b) on the conversion of canola oil to FAME using 5% AlCl3 as catalyst (by wt based on oil) at 110 °C and THF as co-solvent (1:1 methanol to THF by weight). In (a), different molar ratios were 6, 12, 24, 42, and 60. In (b), different reaction time were 6, 18, and 24 h. The tables show the results of statistical analysis using ANOVA.
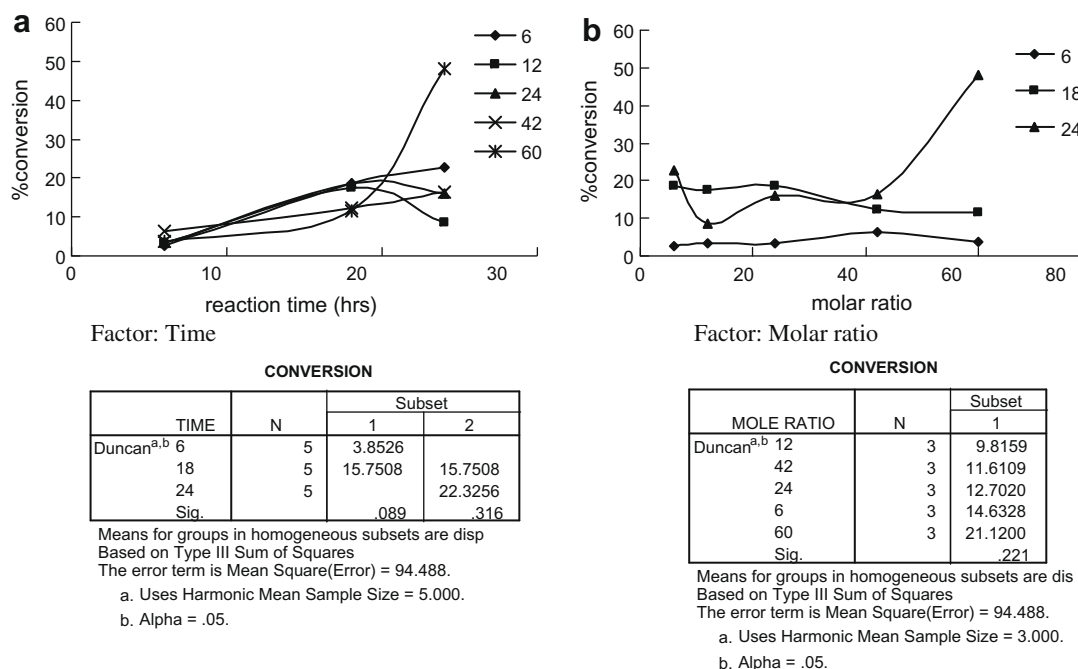
Fig. 5. Effect of reaction time (a) and molar ratio (b) on the conversion of canola oil to FAME using 5% ZnCl2 as catalyst (by wt based on oil) at 110 °C and THF as co-solvent (1:1 methanol to THF by weight). In (a), different molar ratios were 6, 12, 24, 42, and 60. In (b), different reaction time were 6, 18, and 24 h. The tables show the results of statistical analysis using ANOVA.

not vary significantly with increasing molar ratio. This is especially true when the reaction time was only 6 h, where the conversion ranged only from 3% to 6% with molar ratio ranging from 6 to 60.

With the use of $ZnCl_2$, the maximum conversion achieved was only 48%, obtainable a with molar ratio of 60 and a reaction time of 24 h. This conversion is comparable with the use of $AlCl_3$ with 60 molar ratio but with reaction time of only 6 h and even much lower compared to the conversion obtained with $AlCl_3$ with molar ratio of 12 and reaction time of 6 h that resulted in a 83% conversion. It is very clear therefore that $ZnCl_2$ owing to its lesser acidity is far less effective than $AlCl_3$ in catalyzing the transesterification of vegetable oil.
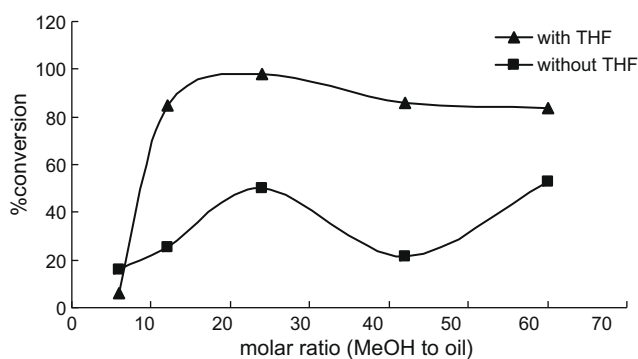
Fig. 6. Effect of added THF as co-solvent in the conversion of canola oil to FAME using 5% AlCl3 as catalyst at 110 °C and 18 h reaction time with increasing methanol to oil molar ratio.

3.3. Effect of THF

Transesterification of vegetable oil with methanol is a two-phase process due to the huge differences in polarities of methanol and oil. THF, added at the level of 1.25 volume per volume of methanol, may act as a co-solvent in the transesterification of vegetable oil with methanol [10]. The addition of THF led to the formation of homogeneous oil-rich transesterification process resulting to faster reaction rates. In our case however, adding 1:1 THF to methanol by weight resulted in a clear homogeneous system when the methanol to oil molar ratio was 24 or greater. With methanol to oil molar ratio of 12, the resulting mixture was a bit cloudy due to the low solubility of the catalyst in the system. Formation of two layers were observed when the methanol to oil molar ratio was only 6 even in the presence of THF. The boiling point of THF is only 2 degrees higher than methanol and hence was recovered together with methanol by distillation.

Fig. 6 shows the effect of adding THF as co-solvent in the transesterification of canola oil with methanol using AlCl$_3$ at 110 °C, 18 h reaction time and varying methanol to oil molar ratios (6–60). The addition of THF decreased the conversion by 61% when methanol to oil molar ratio was only 6. As mentioned above at this molar ratio, the amount of THF (since the amount of THF was based on the amount of methanol used) added was not enough to favor the formation of a single-phase system. Since AlCl$_3$ is more soluble in polar solvents, the methanol-THF phase was enriched with the catalyst. For base-catalyzed transesterification, a catalyst-rich methanol phase is not much of a problem since the very first reaction involved in this process is the generation of methoxide ion from the reaction of the basic catalyst (usually NaOH or KOH) with methanol. On the other hand with the AlCl$_3$ in the methanol-THF phase, activation of the carbonyl carbon of the triglyceride molecules was minimized since this occurs via the electrophilic attack of AlCl$_3$ with the carbonyl oxygen that eventually leads to lower conversion.

At higher molar ratios, the addition of THF resulted in significantly higher conversions as a result of the formation of a one-phase system. In the presence of THF, the mass transfer problem normally encountered in a heterogenous system was eliminated. Moreover, with AlCl$_3$ and triglyceride in the same phase, activation of carbonyl carbon is more favorable eventually leading to higher conversion.

4. Summary and conclusions

The use of AlCl$_3$ and ZnCl$_2$ as catalyst for biodiesel synthesis was reported. AlCl$_3$, being a stronger Lewis acid than ZnCl$_2$, catalyzed

the transesterification of canola oil far more effectively than ZnCl$_2$. It was also demonstrated that AlCl$_3$ could catalyze the esterification of stearic acid suggesting that it is a potential alternative catalyst for biodiesel preparation using cheaper vegetable oil containing high amount of FFA. Statistical analysis showed that the optimum conditions to afford 98% conversion of canola oil to FAME is with the use of 24 methanol to oil molar ratio and reaction time of 18 h at 100 °C in the presence of 5% AlCl$_3$ as catalyst and THF as co-solvent. The added THF minimized the mass transfer problems normally encountered in heterogeneous systems resulting in an increase in conversion. Regardless of molar ratio and reaction time, conversions using AlCl$_3$ had increased with increase in reaction temperature. While statistical analysis showed that the conversion differed significantly with molar ratio and reaction time with the use of AlCl$_3$, conversion using ZnCl$_2$ differed only with reaction time and not with molar ratio.

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