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Transesterification of soybean oil to biodiesel with Zn/I_2 catalyst

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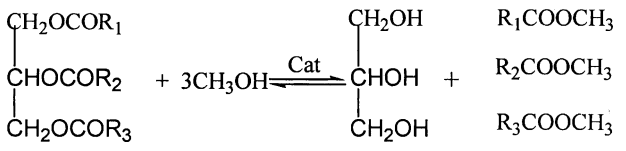
Zn/I_2 was found to be a practical and effective catalyst for the transesterification of soybean oil with methanol. A study for optimizing the reaction conditions such as the molar ratio of methanol to oil, the reaction time and the catalyst amount, was performed. The highest conversion of 96% was obtained under the optimum conditions. Further, the effect of free fatty acids and water in the soybean oil on the catalytic activity of the catalysts was also investigated.

KEY WORDS: iodine; zinc; biodiesel; transesterification.

1. Introduction

As supply of fossil fuels is limited whilst energy demand continues to rise, research is increasingly directed towards alternative renewable fuels. Biodiesel, as an alternative diesel fuel, consisting of long chain fatty acid esters derived from vegetable oils or animal fats, has become more attractive because of its environmental benefits and the fact that it is made from renewable resources [1]. Biodiesel is characterized by excellent properties as diesel engine fuels and thus can be used in compression-ignition (diesel) engines with little or no modifications. Due to its biodegradability and non-toxicity, the production of biodiesel is considered to be an advantage to that of fossil fuels. In addition to this, it also shows a decrease in the emission of CO, SO_x, unburned hydrocarbons and particulate matter during the combustion process [2].

Commercial biodiesel is produced from renewable resources including rapeseed and soybean oil, which are composed of C_{14}–C_{20} fatty acid triglycerides. These triglycerides are converted to the respective alkyl ester and glycerol by transesterification with short chain alcohols, typically methanol. Transesterification of vegetable oils with methanol can be carried out using either basic or acidic catalysts, as illustrated by the following equation.



Normally, most biodiesel is prepared using homogeneous basic catalysts, such as potassium hydroxide, sodium hydroxide, as well as potassium and sodium alkoxides [3–6]. Even though acid-catalyzed process is suitable if the vegetable oils have a high free fatty acid content and more water, the reaction time is very long (48–96 h) even at the boiling point of the alcohol, and a high molar ratio of methanol to oil is required (30–150:1, by mol) [7–9]. Thus, base catalysis is preferred to acid catalyzed routes using sulfonic acid or hydrochloric acid, which are more corrosive with lower activities. Industrially, sodium or potassium hydroxides were usually selected as catalysts, since they are relatively cheap and also very active. However, in this conventional homogeneous method, removal of these base catalysts after reaction is technically difficult and, a large amount of wastewater was produced to separate and clean the catalyst and the products. Besides, the oils should be acid-free and the alcohol anhydrous ($< 1\%$ water) in order to avoid formation of soap and emulsions which make phase separation of the glycerol and methyl esters difficult [10,11]. Therefore, for the development of an environmentally benign process and the reduction of the production cost, a new type catalyst should be introduced. Heterogeneous catalysts could improve the synthesis methods by eliminating the additional processing costs associated with homogeneous catalysts and minimizing the pollutants of production. At the laboratory scale, many different heterogeneous catalysts have been developed to catalyze the transesterification of vegetable oils with methanol [12–16]. For example, commercial hydrotalcite [12], calcium carbonate rock [13], $Na/NaOH/\gamma$–Al_2O_3 [14], modified zeolite [15] and Li/CaO [16] have been found to be efficient heterogeneous catalysts for the transesterification of vegetable oils with methanol; however, they are quite expensive or complicated to prepare, which limited their industrial application. Thus, it is desirable to find more efficient and cheap catalysts for transesterification of triglyceride with methanol in the application of commercial production.

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In recent years, Ramalinga *et al.* [17] reported that iodine could catalyze transesterification of vegetable oils with methanol under a mild condition. But, unfortunately we were unable to get the high conversion according to the procedure described by authors. Our interest in the use of catalyst for biodiesel preparation has prompted us to explore an easily prepare, inexpensive and effective catalyst for the transesterification of vegetable oils.

During the course of our study, we find out that metal/I_2, especially Zn/I_2, can catalyze transesterification of soybean oil with methanol in a highly efficient manner under a mild condition. To our knowledge, the study on Zn/I_2 as an alternative catalyst for biodiesel production has not appeared by far. In this work, the catalytic efficiency of Zn/I_2 in the transesterification reaction of soybean oil was evaluated regarding the conversion of soybean oil to methyl esters. The effects of various reaction variables such as the catalyst loading, the molar ratio of methanol to oil and the reaction time on the conversion to methyl esters were investigated. Furthermore, the influence of free fatty acids and water on the catalytic activity of the catalysts was also investigated, as vegetable oils usually contain water and free fatty acids and these materials may affect the catalytic activity of this system.

2. Experimental

2.1. Catalyst preparation

Metal activation: 50 g metal powder (about 100 meshes) was washed with distilled water (2×50 mL). After decanting the water layer, it was treated with 5% dilute HCl (2×30 mL) under vigorous stirring. The acid was decanted and the metal was treated with distilled water (3×50 mL). Then it was treated with acetone (2×50 mL) to remove the traces of water before being dried in an oven at 373 K.

Iodine was treated by sublimation.

2.2. Transesterification procedures

Commercial edible grade soybean oil was obtained from market and used as received. According to GC (Shimadzu DC-9A) analysis [18], the fatty acid consisted of, 12.3% palmitic acid, 5.8% stearic acid, 26.5% oleic acid, 49.4% linoleic acid and 5.9% linolenic acid. The acid value was less than 0.1 mg KOH/g and the average molecule weight was 874 g/mol, calculated from the saponification value (S.V. = 192.6 mg KOH/g).

A 250 mL two-necked glass flask with a water-cooled condenser was charged with 16.0 g (18.3 mmol, calculated from the average molecular weight of the soybean oil) of soybean oil, different volume of anhydrous methanol and varied amounts of catalyst. The mixture was stirred vigorously and refluxed at 338 K for required reaction time. The progress of the reaction was monitored by ^{1}H-NMR spectroscopy (Bruker, 400 MHz) [19]. Normally, the sample was filtered and the liquid phase was washed three times with an aqueous solution of sodium thiosulfate and a saturated aqueous NaCl solution, respectively. The organic phase was separated by decantation, dried with anhydrous sodium sulfate and submitted to NMR analysis in $CDCl_3$ using TMS as internal standard. The conversion of the soybean oil to a mixture of the methyl esters was determined by the ratio of the signals at 3.68 ppm (methoxy groups of the methyl esters) and 2.30 ppm (α-carbon CH_2 groups of all fatty acid derivatives) according to the reference [19].

3. Results and discussion

The selected metals, and these metals of combination with I_2, as listed in table 1, were screened for their catalytic activity. As the screening experiments were intended for an initial evaluation of the activity of the catalysts, they were conducted under a preliminary set of reaction conditions, which may not have been the optimum set for all the catalysts.

The screening results for the tested catalysts are summarized in table 1. As indicated by the conversion data in table 1, the selected metals can catalyze the transesterification of soybean oil with methanol. Among these metal catalysts tested, Pb showed highest activity toward the transesterification reaction, giving a conversion of 55%, followed by Zn. But the other considered metals, such as Fe, Sn, Cu and Al could not

Table 1
Summary of conversions of soybean oil over various catalysts

Entry	Catalyst	Alcohol	Time (h)	Conversion (%)
1	I_2	CH_3OH	26	28
2	Zn	CH_3OH	26	11
3	I_2/Zn	CH_3OH	26	96
4	Al	CH_3OH	26	8
5	I_2/Al	CH_3OH	26	8
6	Sn	CH_3OH	26	3
7	I_2/Sn	CH_3OH	26	14
8	Ni	CH_3OH	26	7
9	I_2/Ni	CH_3OH	26	6
10	Cu	CH_3OH	26	6
11	I_2/Cu	CH_3OH	26	6
12	Fe	CH_3OH	26	9
13	I_2/Fe	CH_3OH	26	No reaction
14	Pb	CH_3OH	26	55
15	I_2/Pb	CH_3OH	26	No reaction
16	ZnI_2	CH_3OH	26	24
17	NaOH	CH_3OH	3	98

Reaction conditions: methanol/oil molar ratio 42:1, catalyst amount of Zn 5 wt.% and I_2 5 wt.%, reaction temperature 338 K, without co-solvent.

effectively catalyze the reaction; the obtained conversions were in the range of 3–9%.

Furthermore, when these selected metals were used combined with iodine, the catalytic activity changed significantly, especially for Pb and Zn. The catalytic activity of Pb was quenched by iodine, while the catalytic activity of Zn was improved greatly in the presence of iodine. In particular, as shown in table 1, Zn/I_2 can smoothly catalyze the transesterification reaction of soybean oil under the mild conditions, achieving a conversion of 96%, which was almost the same value as that observed in the homogeneous NaOH catalyzed system, except the latter required a shorter reaction time.

For comparison purpose, ZnI_2 was also used as catalyst in the transesterification reaction and the result indicated that the conversion of soybean oil was 24%, which was much lower than that on Zn/I_2, suggesting that the catalytic activity of Zn/I_2 towards the transesterification reaction was not associated with ZnI_2, and consequently the catalytic mechanism of Zn/I_2 seemed to be further studied.

As just discussion above, Zn/I_2 manifested the best catalytic activity. On account of the high activity of the catalyst in the transesterification reaction, the influence of various reaction conditions were studied to optimize the reaction procedure.

The transesterification process consists of a sequence of consecutive reversible reactions where the triglycerides is successively transformed into diglyceride, monoglyceride, and finally into glycerin and the methyl esters. One of the most important variables affecting the conversion to methyl esters is the molar ratio of methanol to vegetable oil. Stoichiometrically, the transesterification of soybean oil requires three moles of methanol for each mole of oil. However, in practice a higher molar ratio is employed in order to shift the reaction equilibrium towards the products side and produce more methyl esters. Figure 1 reflects the effect of molar ratio of methanol to oil on the conversion of soybean oil. As shown in this figure, with increasing methanol-loading amount, the conversion was increased considerably. When the molar ratio was very close to 42:1, the maximum conversion is achieved. But, beyond the molar ratio of 42:1, the excessively added methanol had no significant effect on the conversion. Therefore, the optimum molar ratio of methanol/oil produce methyl esters is approximately 42:1.

In general, the molar ratio is associated with the type of catalyst used. Previous results have shown that an acid-catalyzed transesterification needs a high molar ratio of methanol to oil (30∼150:1) on account of slower reaction rates, while the molar ratio of methanol to oil 6∼15:1 is usually used in base-catalyzed system [1]. However, in this work, such a high proportion of methanol was used to promote high equilibrium conversion of oil to esters, which was also found in the routes catalyzed by acid catalysts such as sulphonic acid [9], suggesting that high catalytic of Zn/I_2 was probably attributed to its acting as Lewis acid in the reaction, and a similar Lewis acid mechanism was taking place. At present, we do not completely understand the mechanism in detail, and so, more studies are required to make a more far-reaching assessment of its catalytic activity.

The rate of transesterification reaction of vegetable oils is strongly influenced by the reaction temperature. However, given enough time, the reaction will proceed to near completion even at room temperature. Commonly, the transesterification reaction is carried out

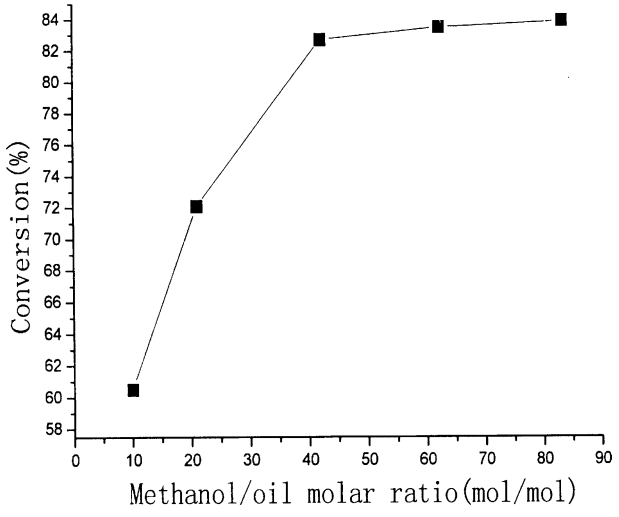

Figure 1. Effect of methanol/oil molar ratio on the conversion of soybean oil to methyl esters. Reaction conditions: catalyst amount of Zn 5 wt.% and I_2 2.5 wt.%, reaction time 16 h, reaction temperature 338 K, without co-solvent.

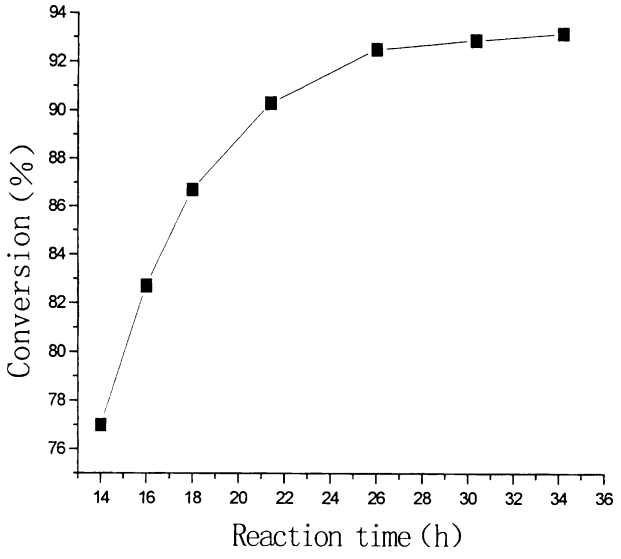

Figure 2. Effect of reaction time on the conversion of soybean oil to methyl esters. Reaction conditions: methanol/oil molar ratio 42:1, catalyst amount of Zn 5 wt.% and I_2 2.5 wt.%, reaction temperature 338 K, without co-solvent.

close to the boiling point of methanol (about 338 K) at atmospheric pressure. Figure 2 graphically illustrates the change of the conversion as a function of reaction time. As can be seen from the graph, the conversion was increased with the increase of the reaction time between 14 and 26 h, and thereafter remained nearly constant as a representative of a nearly equilibrium conversion. On the basis of these results, the optimum reaction time for the synthesis of biodiesel is considered to be around 26 h at reflux of methanol.

The effect of catalyst amount on the conversion was investigated at 42:1 molar ratio of methanol to soybean oil at reflux of methanol for 26 h. The catalyst amount of I_2 was varied in the range of 0.2–7.0%, while the Zn amount remained a constant of 5 wt.%. These percentages are weight fractions of the oil supplied for this reaction. The reaction profile of figure 3 indicated that the transesterification reaction was strongly dependent upon the catalyst applied. Without addition of a catalyst, the transesterification procedure did not occur, and the presence of the catalyst really increased the reaction rate. As shown in figure 3, the conversion was increased with increase of I_2 amount from 0.2 to 5 wt.%. However, with further increase of the I_2 amount the conversion was decreased. Therefore, the optimum catalyst amounts of Zn and I_2 were found, respectively to be 5 wt.% in this system.

Because of the fact that the oil and methanol are immiscible, the reactants initially form a three-phase system, oil/methanol/catalyst. Accordingly, the transesterification reaction is diffusion-controlled and poor diffusion between the phases results in a slow rate. As expected, the initial lag phase is usually attributed to transport effects required transferring the methanol into the oil phase [20]. In order to speed up the reaction rate, Boocock *et al.* [21] suggested the addition of tetrahydrofuran (THF) as a co-solvent to minimize mass transfer resistance. To overcome the mixing problems in these experiments, appropriate co-solvents, such as dimethyl sulfoxide (DMSO) and THF, were introduced. From the result shown in figure 4, the conversion was increased by 10% under the same conditions with the addition of DMSO as a co-solvent, indicting DMSO was the more effective co-solvent. Optimum loading amount of DMSO was found to be 6:1 soybean oil to DMSO molar ratio.

A co-solvent like DMSO produces an oil-dominant one-phase system in which the transesterification reaction was speeded up. In the absence of DMSO, the low oil concentration in methanol slows down the reaction due to the slow dissolution of oil in methanol and this is also reflected in an initial lag phase [22]. The solubility of DMSO in methanol and oil makes it a mutual solvent and thus mutual oil–methanol solubility could be increased, resulting in the increase of reaction rate. However, in contrast with the results in the literature [21], THF did not increase the conversion but resulted in a drop of the conversion as illustrated in figure 4, mostly owing to that THF deactivated the catalyst.

Additionally, free fatty acids and water present in soybean oil also affect the conversion to methyl esters. Although the reaction rate of alkali-catalyzed transesterification of vegetable oils is much faster than that of acid-catalyzed reaction, the alkali catalysts are extremely negatively affected by the free fatty acid components and water present in the reaction system. The free fatty acids react with an alkali catalyst to form soaps, while the presence of water could cause ester saponification under alkaline condition [23,24]. Saponification reduces catalytic efficiency and the resulting soaps result in the formation of emulsions. Emulsion formation creates difficulties in downstream recovery and purifi-

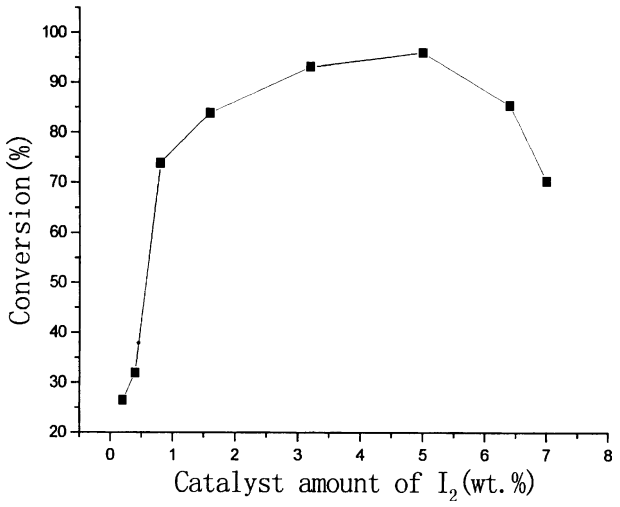

Figure 3. Effect of catalyst amount on the conversion of soybean oil to methyl esters. Reaction conditions: methanol/oil molar ratio 42:1, catalyst amount of Zn 5 wt.%, reaction time 26 h, reaction temperature 338 K, without co-solvent.

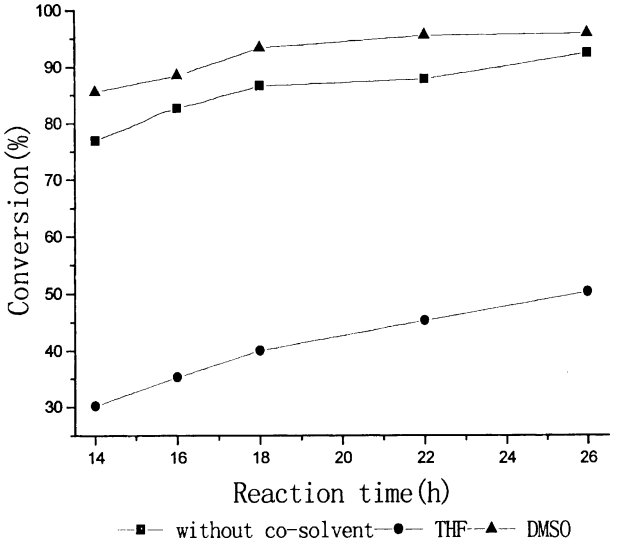

Figure 4. Effect of co-solvent on the conversion of soybean oil to methyl esters. Reaction conditions: methanol/oil molar ratio 42:1, catalyst amount of Zn 5 wt.% and I_2 2.5 wt.%, reaction temperature 338 K.

cation of the methyl esters. Thus, the dehydrated vegetable oil with less than 1 mg KOH/g free fatty acids and anhydrous alcohol are necessary for commercially viable alkali-catalyzed systems. This requirement is likely to be a significant limitation to the use of waste cooking oil as a low-cost feedstock in base-catalyzed system. However, methodologies based on acid-catalyzed reactions have the potential to achieve this since acid catalysts do not show measurable susceptibility to free fatty acids and water. Despite its insensitivity to free fatty acids and water in the feedstock, the acid-catalyzed transesterification has been largely ignored because of its relatively slower reaction rate. Freedman *et al*. [25] investigated the transesterification of soybean oil with methanol using 1 wt.% concentrated sulfuric acid (based on oil) as catalyst and found that at 383 K and a molar ratio of 30:1 methanol to oil, it took reaction time of 69 h to obtain more than 90% oil conversion to methyl esters. To identify the high catalytic activity of Zn/I_2, the effects of the free fatty acids and water in reactants on the conversion of soybean oil were also investigated. Experimental runs were made with the addition of water and free fatty acid to the reactants. These data shown in table 2 indicated that the conversion of soybean oil was decreased with the increase of the amount of free fatty acids and water added; however, the acid value and water content of the feedstock had not a great effect on the conversion. Even though the acid value and the water content were high, such as 3 mg KOH/g and 1.5 wt.%, the conversion to methyl esters still reached 85%. However, many investigators have noted that more than 0.3 wt.% water or more than 1 mg KOH/g of free fatty acids in this system significantly reduced the conversion in base-catalyzed reactions [25,26]. Thus the catalytic activity of the catalyst is not significantly affected by water and free fatty acids, and therefore it may be a promising alternative catalyst for biodiesel production when the feedstock does not meet the base-catalyzed process.

Table 2
Effect of water content and acid value on conversion of vegetable oil to methyl esters

Entry	Water content (wt.%)	Acid value (mg KOH/g)	Conversion (%)
1	0.1	0.2	96.0
2	1.0	0.2	94.0
3	1.5	0.2	95.6
4	3.0	0.2	95.0
5	1.0	1.0	92
6	1.0	1.5	90
7	1.0	2.5	87
8	1.5	3	85

Reaction conditions: molar ratio of soybean oil to methanol 42:1, catalyst amount of Zn 5 wt.% and I_2 5 wt.%, reaction time 26 h, reaction temperature 338 K, without co-solvent.

4. Conclusions

Biodiesel, consisting of long chain fatty acid esters and produced by the transesterification of vegetable oils, is a promising alternative fuel to diesel regarding the limited resources of fossil fuel and the environmental concerns. In the present work, Zn/I_2 was firstly found to be a practical and effective catalyst for the production of biodiesel. In order to maximize the conversion to methyl esters, the optimum methanol to oil molar ratio, reaction time and the amount of catalyst were determined. The presence of the co-solvent DMSO in the reaction mixture substantially increased the conversion of soybean oil. While the transesterification reaction is highly sensitive to moisture and free fatty acids, special precautions need not be taken to exclude moisture or acid from the system with this catalyst. The highest conversion of 96% was obtained with Zn/I_2 as a catalyst under the optimum condition. The notable advantages of this method are: operational simplicity, mild reaction conditions and high conversion.

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