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Investigation of Biodiesel Production from Canola Oil using Mg-Al Hydrotalcite Catalysts

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Biodiesel produced by the transesterification of vegetable oils is a promising alternative fuel to diesel because of limited fossil fuel resources and environmental concerns. The use of heterogeneous catalysts greatly simplifies the technological process by facilitating the separation of the post-reaction mixture. The purpose of the present work was to examine a heterogeneous catalyst, in particular, Mg-Al hydrotalcites, to produce methyl esters of canola oil. In this study, the transesterification of canola oil with methanol was studied in a heterogeneous system, using Mg-Al hydrotalcites as solid base catalysts. The results showed that methanol is the best alcohol for this reaction condition. The highest triglyceride conversion rate of 71.9% was achieved after 9 h of reaction at 60 °C, with a 6:1 molar ratio of methanol to canola oil and a 3 wt% catalyst with 125-150 μm particles.

Key Words: Biodiesel, transesterification, Mg–Al hydrotalcite, heterogeneous base catalyst.

Introduction

Biodiesel, monoalkyl esters of fatty acids derived from vegetable oils or animal fats, is known as a clean and renewable fuel. Biodiesel is usually produced by the transesterification of vegetable oils or animal fats with methanol or ethanol.[1] When methanol is used, the transesterification reaction is referred to as methanolysis. Methanolysis of triglyceride is represented in Figure 1. The transesterification reaction can be catalyzed by both homogeneous and heterogeneous catalysts. The homogeneous catalysts include alkalis and acids. The most commonly used alkali catalysts are sodium hydroxide and potassium hydroxide.[2]

The acid-catalyzed process often uses sulfuric acid and hydrochloric acid as catalysts; however, the reaction time is very long (48-96 h), even at reflux of methanol, and a high molar ratio of methanol to oil is needed (30-150:1, by mole). Potassium hydroxide, sodium hydroxide, and their carbonates, as well as potassium and sodium alkoxides, such as $NaOCH_3$, are usually used as base catalysts for this reaction. As the catalytic activity of a base is higher than that of an acid, and acid catalysts are more corrosive, the base-catalyzed process is preferred to the acid-catalyzed one, and is thus most often used commercially.

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However, in the conventional homogeneous manner, removal of these base catalysts is technically difficult and a large amount of wastewater is produced to separate and clean the catalyst and the product. Therefore, conventional homogeneous catalysts are expected to be replaced in the near future by environmentally friendly heterogeneous catalysts, mainly due to environmental constraints and simplification of the existing processes.[3]

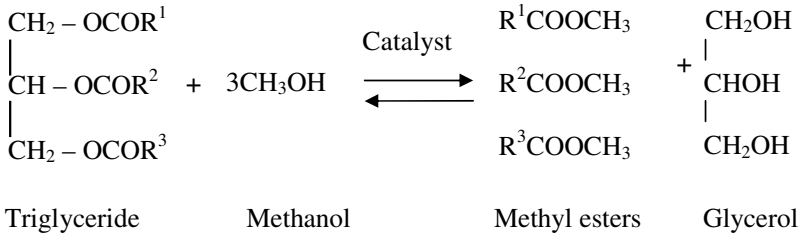

Figure 1. General equation for the transesterification of triglyceride with methanol.

Many different heterogeneous catalysts have been developed to catalyze the transesterification of vegetable oils to prepare fatty acid methyl esters. For example, Kim et al.[4] prepared a solid superbase of $Na/NaOH/\gamma\text{-}Al_2O_3$ that showed almost the same catalytic activity under optimized reaction conditions as the conventional homogeneous NaOH catalyst. Xie et al.[5] achieved 87% conversion when the reaction was carried out at reflux of methanol for transesterification of soybean oil using KNO_3/Al_2O_3 as a solid base catalyst. Recently, Wang et al.[6] reported that the yield of biodiesel produced with SrO as a catalyst was in excess of 95% within 30 min at temperatures below 70 °C.

In particular, Mg-Al hydrotalcites are solids with interesting basic properties that have shown good activity in transesterification reactions. The hydrotalcite $Mg_6Al_2(OH)_{16}CO_3.4H_2O$ has attracted much attention during the development of new environmentally friendly catalysts. Their chemical composition can be represented by the general formula $[M^{2+}_{(1-x)}M^{3+}_x(OH)_2]^{x+}(A_{x/n})^{n-}yH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations respectively, A^{n-} is an n-valent anion, and x usually has a value between 0.25 and 0.33. Synthetic hydrotalcite-like compounds have found a variety of uses in heterogeneous catalysis, polymer processing, and pharmacy. They are also known as good adsorbents and anion exchangers.[7,8] In this study, calcined Mg-Al hydrotalcites were adopted for methanolysis of canola oil and the optimum reaction conditions were investigated.

Experimental

Catalyst preparation: Hydrotalcites were prepared by the co-precipitation method. Firstly, 150 mmol of $(Mg(NO_3)_2)$ and 50 mmol of $(Al(NO_3)_3)$ were dissolved in 200 cm^3 of distilled and deionized water. Then, this solution was fed at the rate of 5 cm^3/min into a 400-cm^3 aqueous solution of 400 mmol of Na_2CO_3, which was then poured into a conical flask and pre-heated to 60-63 °C. During co-precipitation, the slurry was vigorously stirred with a magnet bar and kept at pH 10 by the drop-wise addition of a 1-M solution of NaOH. After complete addition of the metal nitrates solution, the suspension was stirred at 60-63 °C for 1 h, followed by ageing for 18 h, without stirring, at the same temperature. The synthesized solid was filtered out, rinsed 7 times with 750 $cm^3$of water, and air-dried at 80 °C for 16 h. The dried solid was ground into a fine powder, which was further calcined in air at 500 °C for 16 h to produce hydrotalcite.

Transesterification reaction: Commercial edible grade canola oil was obtained from a market. A 500-cm^3 three-necked glass flask with a water-cooled condenser was charged with 50 g of canola oil, different volumes of anhydrous alcohol, and varied amounts of Mg-Al hydrotalcite catalysts. The mixture was refluxed at the required temperature for 9 h under stirring at 500 rpm. After the reaction, the solid catalyst was separated by filtration. The liquid was put into a separating funnel and was kept at ambient temperature for 24 h, after which 2 liquid phases appeared. The upper layer was biodiesel and the lower layer was glycerol. The conversion of canola oil was calculated from the quantity of total glycerol in the product. The procedure was carried out according to the AOCS Official Method Ca 14-56.

Results and Discussion

The effects on biodiesel production of the methanol/canola oil molar ratio, type of alcohol and co-solvent, reaction temperature, particle size, and mass ratio of catalyst to oil were investigated. The transesterification process consists of a sequence of 3 consecutive reversible reactions in which the triglyceride is successively transformed into diglyceride, monoglyceride, and finally into glycerin and fatty acid methyl esters. The molar ratio of methanol to canola oil is an important factor that affects the conversion to methyl esters. Stoichiometrically, 3 moles of methanol are required for each mole of triglyceride, but in practice a higher molar ratio is employed in order to drive the reaction towards completion and produce more methyl esters as products. Figure 2 reflects the effect of methanol/oil molar ratios on the conversion. As shown in this figure, with an increase in the methanol-loading amount, conversion was decreased. The highest conversion rate of 63.1% was achieved when the molar ratio was 6:1.

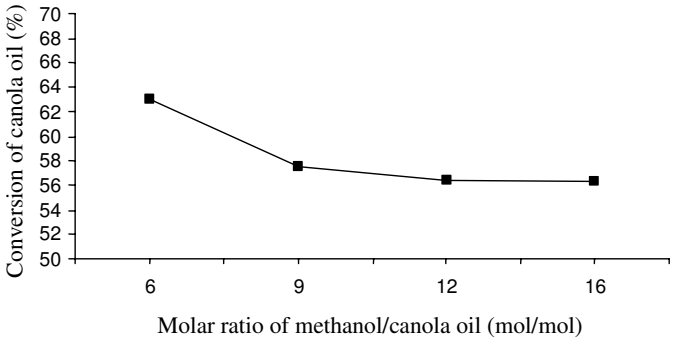

Figure 2. Conversion of canola oil as a function of the methanol/oil molar ratio. Reaction conditions were as follows: Catalyst amount: 3 wt%; reaction time: 9 h; temperature: 60 °C; particle size: 150-177 μm.

The effect of the reaction temperature on the conversion of canola oil was studied. As shown in Figure 3, the transesterification reaction was not strongly dependent upon temperature. If the reaction temperature exceeds the boiling point of methanol, the methanol will vaporize and form a large number of bubbles, which inhibit the reaction on the 3-phase interface. The highest conversion rate of 63.1% was achieved when the reaction temperature was 60 °C.

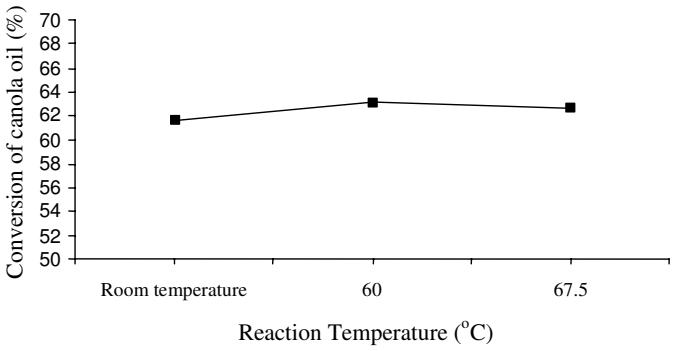

Figure 3. Conversion of canola oil as a function of reaction temperature. Reaction conditions were as follows: Catalyst amount: 3 wt%; reaction time: 9 h; methanol/canola oil molar ratio: 6:1; particle size: 150-177 μm.

The influence of particle size was studied using 3 different particle size fractions: 150-177, 125-150, and $<$ 125 μm. As shown in Figure 4, conversion of canola oil increased as particle size decreased from 150-177 μo 125-150 μm. The conversion of canola oil was the lowest using the smallest particle size ($<$ 125 μm). The highest conversion rate of 71.9% was achieved when particle size was 125-150 μm.

To investigate the effects of different alcohol types on the transesterification of canola oil, methanol, ethanol, and isopropyl alcohol (IPA) were compared. As shown in Figure 5, the highest conversion of canola oil was observed when methanol was used in the transesterification reaction. Lower conversion rates of canola oil were observed by using ethanol and IPA. These results suggest that steric effects control these catalytic activities.

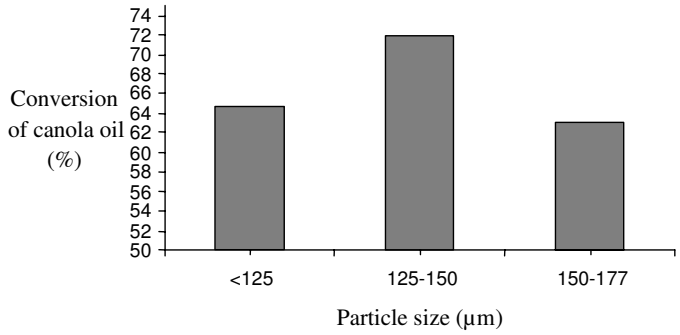

Figure 4. Conversion of canola oil as a function of particle size. Reaction conditions were as follows: Catalyst amount: 3 wt%; reaction time: 9 h; methanol/canola oil molar ratio: 6:1; temperature 60 °C.

Generally, the co-solvent increases the rate of reaction by making the oil soluble in methanol, thus increasing the contact of the reactants. In order to conduct the reaction in a single phase, co-solvents like n-hexane and IPA were tested. As shown in Figure 6, the presence of co-solvents, such as n-hexane and IPA, in the reaction mixture decreased the conversion of canola oil.

The effect of the amount of catalyst on the conversion of canola oil was studied. The catalyst amounts tested were 3%, 6%, and 9%. These percentages were weight fractions of the oil supplied for these reactions. As shown in Figure 7, when the catalyst amount increased, the conversion of canola oil increased. Although the highest catalyst amount resulted in the highest conversion of canola oil, the cost of the catalyst has a crucial role in the economics of biodiesel.

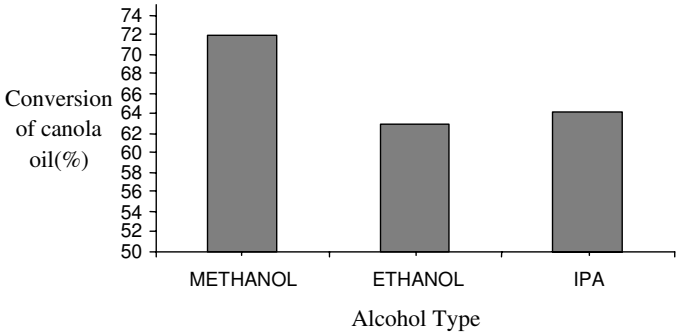

Figure 5. Conversion of canola oil as a function of alcohol type. Reaction conditions were as follows: Catalyst amount: 3 wt%; reaction time: 9 h; alcohol/canola oil molar ratio: 6:1; temperature: 60 °C; particle size: 125-150 μm.

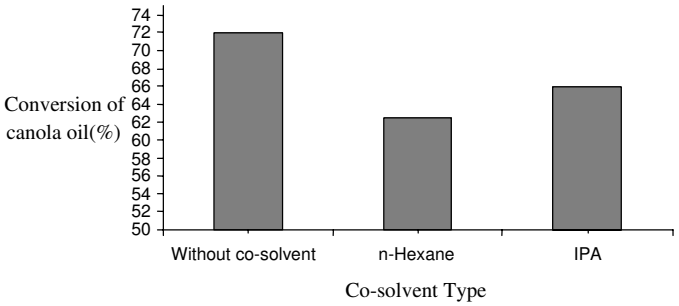

Figure 6. Conversion of canola oil as a function co-solvent type. Reaction conditions were as follows: Catalyst amount: 3 wt%; reaction time: 9 h; alcohol/canola oil molar ratio: 6:1; temperature: 60 °C; particle size: 125-150 μm; co-solvent content: 10 wt%.

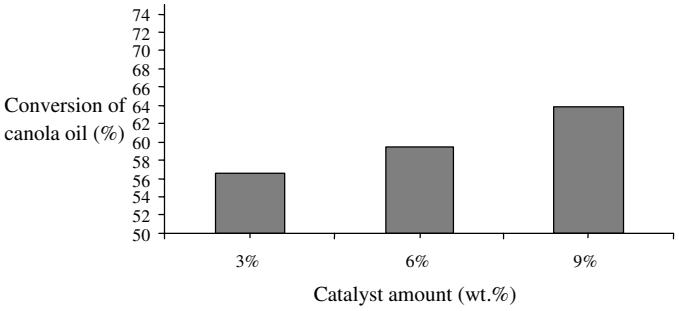

Figure 7. Conversion of canola oil as a function catalyst amount. Reaction conditions were as follows: Reaction time: 9 h; methanol/canola oil molar ratio: 12:1; temperature: 60 °C; particle size: 150-177 μm.

Conclusion

In this study the transesterification of canola oil with methanol was studied in a heterogeneous system using Mg-Al hydrotalcites as solid base catalysts. Hydrotalcites were prepared by co-precipitation of magnesium and aluminum hydroxides from their nitrate solutions using an aqueous solution of sodium carbonate as

the precipitating agent. The effects on biodiesel production of the methanol/canola oil molar ratio, type of alcohol and co-solvent, reaction temperature, particle size, and mass ratio of catalyst to oil were investigated. Our results showed that methanol was the best alcohol for this reaction condition and using n-hexane and IPA as co-solvents decreased the product yield. The highest triglyceride conversion rate of 71.9% was achieved after 9 h of reaction at 60 °C, with a 6:1 molar ratio of methanol to canola oil and a 3 wt% catalyst with 125-150 μm particles.

In comparison with the conventional KOH homogeneous catalyst, transesterification of canola oil with methanol was performed. The triglyceride conversion rate of 99% was achieved after 1 h of reaction at 60 °C, with a 6:1 molar ratio of methanol to canola oil and 1 wt% catalyst. The Mg-Al hydrotalcite heterogeneous base catalysts showed less activity compared to the conventional homogeneous KOH catalyst. With the use of modified hydrotalcites leading to higher basicity, it would be expected to improve conversion to greater than 90%, which would be of commercial interest.

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