



Biodiesel Production from Methanolysis of Refined Vegetable Oil through KOH/zeolite Catalyst

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Abstract In this study, bentonite based catalyst was prepared by impregnation methods in potassium hydroxide solution (35 wt.%). The catalysts were calcined at 500°C for 3 h. The best reaction conditions in the presence of KOH/bentonite were determined while modifying the catalyst to soybean oil ratio and the reaction time. Bentonite was proved to enhance the transesterification reaction, which promotes the transformation of KOH to the catalytically active methoxide species. The influence of the operating variables such as reaction time, methanol: soybean oil molar ratio and catalyst concentration on the reaction yield was evaluated. The highest methyl ester yield (94.5%) was obtained for a reaction time of 15 h, a catalyst to soybean oil ratio of 0.6 wt.%, and a methanol to soybean oil molar ratio of 1:12.

Keywords Transesterification, Methanolysis, Bentonite, Soybean oil, Biodiesel

1. Introduction

Due to the increasing demand for energy together with the expected depletion of fossil fuels resources and increasing the environmental concerns associated with fossil fuel consumption, many research have been carried out in order to find a new alternative renewable energy sources to substitute these dwindling energy reserves [1-4]. Moreover, the global warming due to greenhouse gases emissions prompted the efforts to explore new sources of energy. Therefore, biodiesel production is receiving considerable attention nowadays because biodiesel is a promising alternative fuel to conventional diesel [5], is renewable, biodegradable, and produces less CO, hydrocarbons and particulates emissions than petroleum based diesel [6, 7]. It is generally produced by alkaline catalyzed trans-esterification of vegetable oils or animal fats with monohydric low molecular weight alcohols [8, 9]. Globally, there are more than 350 oil bearing crops identified as potential sources for biodiesel production[10]. The most common oils include soybean[11], corn, used fried oil, sunflower, olive [12], rapeseed [13], castor, lesquerella [14], *Jatropha curcas* [15], *karanja*, *Madhuca indica* (Mahua) and *Salvadora* [16], palm oil [17] and etc. Biodiesel derived from these sources can be defined as mono-alkyl esters of long chain fatty acids [18]. Types of oils selected for biodiesel feed stocks depend upon their availabilities and quality of the derived biodiesels [19]. Transesterification process is boosted with the use of catalyst that also aids in achieving better yields. Three types of catalysts used are namely acidic, alkaline and enzymes [20]. Potassium hydroxide as a homogenous catalyst is some of the commonly used alkaline catalysts [21]. However, homogeneous catalysts have some drawbacks, e.g. they produce large amount of waste water [22]. On the other hand, heterogeneous catalysts are less corrosive, more environmentally friendly, safer, cheaper and they can be easily recovered, regenerated and reused [23].



In this study, soybean oil was used as the raw material for methanolysis to synthesize biodiesel using a reflux reaction system to which bentonite was added as a base catalyst in the KOH catalyzed transesterification. The objective of this study was to investigate the effects of bentonite on the transesterification process.

2. Experimental Procedures

2.1. Materials and Methods

Refined soybean oil was purchased from a local market. Methanol (purity 99.8%), potassium hydroxide (85%, pellets) were supplied by Sigma Aldrich.

2.2. Catalyst Preparation

Bentonite was used as support to prepare of KOH/bentonite catalysts with KOH loadings according to the wet impregnation method [24]. Appropriate amount of KOH (6.33 g for 35 wt. % respectively) were dissolved in 50 mL of distilled water. Each aqueous solution of KOH was slowly added to 10 g of the bentonite support. The resulting slurry was then stirred (300 rpm) at 80 °C for 2 h. After impregnation, the catalysts were dried at 80°C overnight and then calcined at 500°C for 3 h at a heating rate of 0.5 °C/min.

2.3. Preparation of Free Fatty Methyl Ester

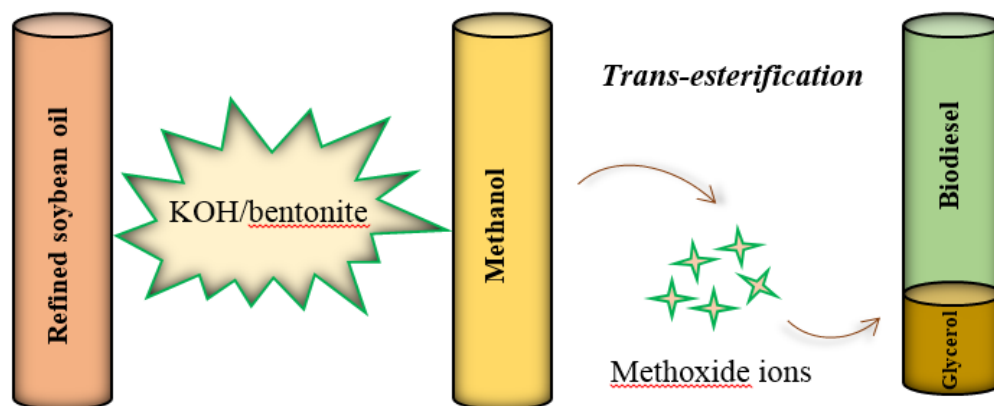


Figure 1: A schematic of the transesterification process

50g of soybean oil and a predetermined amount of catalyst were added to a 3-neck flask reactor and stirred at 60°C. Separately, KOH/bentonite as the catalyst (0.2, 0.4, 0.6 and 0.8) were dissolved in a predetermined amount of anhydrous methanol, at a molar ratio of methanol:soybean oil of (1:6, 1:8, 1:10, 1:12 and 1:14). The bentonite loaded by KOH-methanol solution was immediately added to the reactor and stirred vigorously at 60°C for (3, 6, 9, 12, 15 and 18 h). After cooling to room temperature (25°C), the phases were separated by centrifugation. The upper layer containing the desired product was collected and the residual methanol evaporated under low pressure at 65°C (fig. 1). This crude biodiesel was purified by water washing [25], and the green diesel content (wt.%) of the refined biodiesel, which represents the purity of biodiesel, was measured by gas chromatography. The biodiesel yield was evaluated through the eq. (1)[26].

$$\text{Biodiesel yield (\%)} = \frac{\text{Final weight of refined biodiesel}}{\text{Initial weight of soybean oil}} \times 100 \quad (1)$$

Table 1: Properties and fatty acid composition of the soybean oil

Details of GC analysis	
GC type	Agilent HP 6890
Column	HP 1 crosslinked methyl siloxane
Detector	Flame ionization detector
Initial	125°C



temperature
 Temperature 15 °C/min for 10 min
 ramp
 Final 275°C

Fatty acid	Composition (%)
Palmitic acid (C16:0)	10.5
Stearic acid (C18:0)	3.6
Oleic acid (C18:1)	23.5
Linolic Acid (C18:2)	54.7
Linolenic acid (C18:3)	7.1
Other acids	0.6

3. Results and Discussion

3.1. Effect of Catalyst Dosage on the Biodiesel Yield

As Fig. 2, the green diesel contents increased with the increasing amounts of catalyst, while the biodiesel yields decreased. This result shows that the reaction conversion was increased at low added levels of KOH. However, the increase of catalyst led to the aggravation of the saponification at higher levels. The biodiesel contents and the biodiesel yields of reaction with bentonite were higher than those of which without bentonite when the same catalyst dosage was used. Fig. 2 shows that biodiesel yield of the transesterification with bentonite decreased more significantly than in the case without bentonite as the catalyst dosage was increased. This observation reflects the fact that the introduction of bentonite improved the catalytic activity of KOH, which resulted in a lower catalyst dosage needed to generate a given level of transesterification. Additional catalyst, however, the formation of the gelatinous substance was another important reason for the declining production of biodiesel. The biodiesel content of transesterification with bentonite exceeds 94.5% when the catalyst dosage was only 0.6 wt.%. The biodiesel yield was reduced from 88% as a result of the increased catalyst dosage. In short, the presence of bentonite reduced the catalyst dosage and increased its effectiveness in generating the biodiesel.

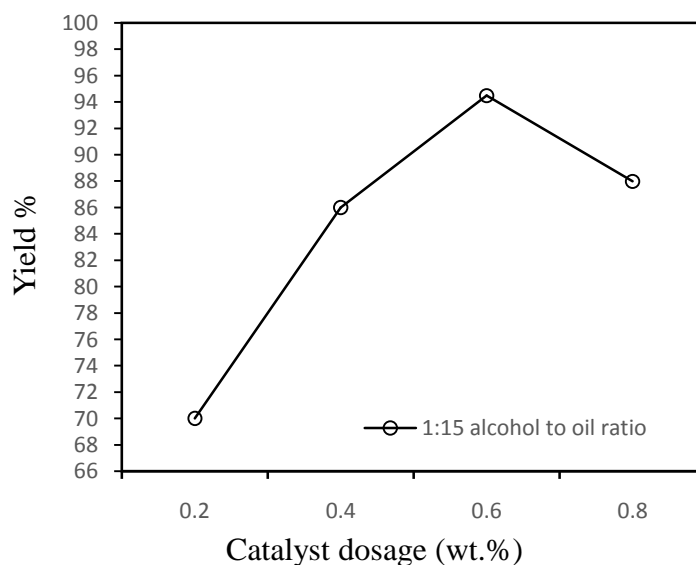


Figure 2: Effects of catalyst dosage on biodiesel yield of transesterification with KOH/bentonite



3.2. Effect of methanol/oil molar ratio

Methanol/ soybean oil molar ratio strongly affects the biodiesel yield. Excess methanol increases the conversion of oil, since transesterification is an equilibrium reaction. However, excess methanol can also increase the energy consumption needed for the recovery of methanol [27, 28], and the catalyst concentration based on total mass decreased with the increase of methanol/oil molar ratio, which led to the decrease of the reaction rate and conversion. The experimental results fig. 3 shows that the highest FAME yield 94.5% was reached when the methanol/ soybean oil molar ratio was 1:12. Because of the adsorption of methanol by bentonite the optimal ratio was higher than 1:10 which is a widely accepted optimal ratio in the traditional homogeneous base-catalyzed transesterification reaction [29].

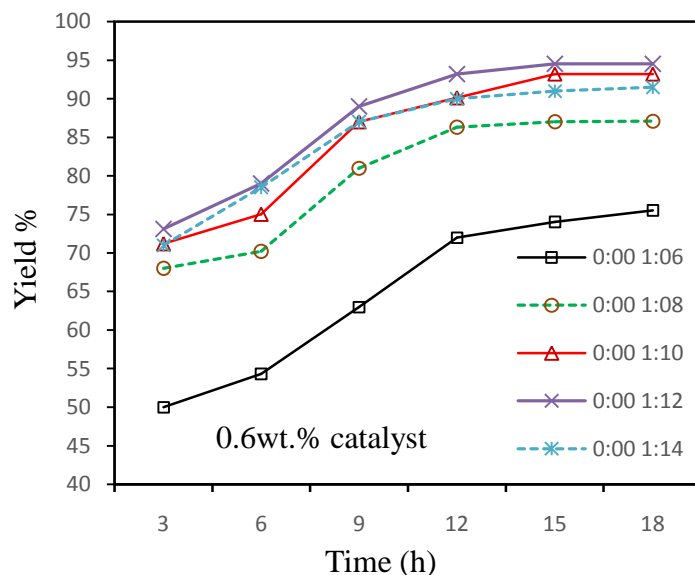


Figure 3: Effect of methanol/ soybean oil molar ratio on biodiesel yield of transesterification with KOH/bentonite

3.3. Effect of reaction time on biodiesel yield

Reaction time plays a significant role in the transesterification of triglycerides [30]. Fig. 2 clearly shows that the FAME yield increased from 73.1% to 94.5% as the reaction time was increased from 3 to 18 h. In particular, the results showed that within the time range 3-15 h, the biodiesel yield increased up to 21.4%. With a further increase in the reaction time, there wasn't any significant change in the biodiesel yield as the equilibrium conversion had been attained. It was clearly documented in literature that the transesterification reaction is slow at the beginning due to a poor dispersion and mixing of alcohol into the oil resulting in lower FAME yield. Afterward, the reaction proceeds rapidly, the yield reaches a maximum and remains constant [31]. The optimum conditions for the transesterification of soybean oil in the presence of KOH/bentonite (35 wt.%) were a catalyst to oil ratio of 0.6 wt.%, a methanol to oil ratio of 1:12 and a reaction time of 15 h.

4. Conclusion

In the present work, bentonite based catalyst was prepared from KOH by impregnation methods. Bentonite was impregnated with KOH loadings to prepare a KOH/bentonite catalysts. Bentonite as a base catalyst for biodiesel synthesis, which promoted the transformation of KOH to the catalytically active methoxide species. The catalyst provided the maximum biodiesel yield at 94.5% obtained in 15 h reaction time at reaction temperature of 60°C, catalyst dosage 0.6 wt.%, methanol to soybean oil molar ratio of 1:12 and stirring speed of 300 rpm.

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