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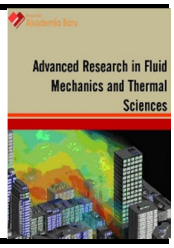

Influence of Operating Variables on the In-Situ Transesterification using $CaO/Al_2(SO_4)_3$ Derived from Waste

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ABSTRACT

The purpose of this research project is to investigate the effects of amount of catalyst, the ratio of solid to methanol and different temperature on the biodiesel yield. Solid coconut waste and heterogeneous catalyst derived from the waste, which is calcium oxide (CaO) are used to produce biodiesel and also examine the kinetics of the reactive extraction. In this project, the heterogeneous catalyst is produced by combining solid coconut waste and egg shells and finally treating it with $Al_2(SO_4)_3$. Then, the mixture of wastes was calcinated under high temperature. Then, solid coconut waste in situ transesterification experiment were conducted at different amount of catalysts (2-6wt%), temperature (50-65°C) and methanol to oil ratio (6:1 – 12:1). The optimum parameters were the solid to methanol ratio, temperature and mixing speed which were at 1:10, 60 °C and 350 rpm respectively with highest yield of 47 wt%. The result proves that the biodiesel conversion increase with methanol, but the reaction did not change and decrease after achieving certain percentage of methanol.

1. Introduction

Biodiesel is generally considered as renewable sources as its primary feedstock is from natural resources which either a vegetable oil or animal fat. The use of biodiesel able to preserve the environment since the carbon content in the oil itself originates from carbon dioxide in the air. As a result, it contributed less to global warming compared with fossil fuels. Thus, the vast application of biodiesel in industrialization and mobilization are preferred based on its advantages. Basically, the properties of biodiesel are like the petroleum based, but it is more environmental preservation since it is biodegradability and low emission of carbon monoxide profile. It likewise contributes to less air pollution as it originates from renewable sources, and is biodegradable securing the environment.

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Biodiesel is often produced from vegetable oil e.g. soybean, palm and sunflower oil or waste animal fats which comprises of a long chain alkyl mainly methyl, ethyl, or propyl esters according to Senthur *et al*., [1, 2]. These fatty acids or unsaturated fats are elements that can support combustion, and have varied properties which are based on the arrangement, bonding and the number of hydrogen and carbon atoms. Besides, vegetable oils are the cheapest and can easily get. The characteristic which has high viscosity can be reduced by undergo several processes to use them in normal engines which include, pyrolysis, emulsification and transesterification [3].

The most successful way to produce biodiesel is by transesterification method which includes the use of vegetable oil and animal fats along with homogenous catalyst in the presence of alcohol [4]. However, the use of homogeneous catalysts will lead to soap formation, the catalyst cannot be reused, and produce large amount of wastewater hence increase the cost for biodiesel production [5, 6]. So, the way to overcome this problem is by using heterogeneous catalyst. Waste materials such as coconut waste and egg shells have been selected as a source of heterogenous catalysts for biodiesel production [7]. Waste catalyst such as eggshell, animal bones, shrimp and crab shells are examples of catalyst that has calcium oxide composition [8]. These heterogeneous catalysts are non-corrosive, do not produce soap and can easily separate from biodiesel product. They can also be reused, has higher selectivity and can be designed for better performance. In addition, the usage of these catalysts can contribute to recycling of waste in effective manner.

The conventional method, where the oil is first extracted from the solid matrix followed by transesterification of the oil is a long process. In this study, reactive extraction or in situ transesterification was used to produce biodiesel. In the in-situ transesterification, extraction and transesterification occurs in the same setup [9]. Reactive extraction is a direct process where all the solid, seed and liquid, solvent and catalyst are mixed in one phase to get a higher yield of methyl ester or biodiesel [10, 11].

In this study, batch in situ transesterification was studied using heterogeneous catalyst. Calcium Oxide (CaO) were obtained from solid coconut waste and egg shells and were chemically treated with $Al_2(SO_4)_3$. Solid coconut waste in situ transesterification experiment were conducted at different amount of catalysts (2-6wt%), temperature (50-65°C) and methanol to oil ratio (6:1 – 12:1) to improve the biodiesel yield.

2. Materials and Methods

2.1 Materials

Coconut waste and egg shells were collected from a shop which produces coconut milk at Pasar Besar Gombak, Malaysia. Methanol and n-Hexane was bought from Sigma Aldrich sdn bhd. The catalyst was extracted from the mixing of coconut waste and egg shell with a ratio 5:1 through the process of calcination. The catalyst produce is then chemically treated with $Al_2(SO_4)_3$ to enhances the yield.

2.2 Preparation of Catalyst

The coconut waste was first dried overnight at temperature of 90°C in an oven. Meanwhile, the egg shells were cleaned with water to remove fines and dirt, and dried at the same time with the coconut waste. After drying, the egg shells were crushed into small pieces to mix with the coconut waste with a ratio of 5:1. Then, calcination was done as the final step of extracting the catalyst CaO from the waste. The dried coconut waste was put in an aluminum foil and into the furnace at 900°C

for 4 hours. After that, it is left to cool inside the furnace for 5 hours and then cooled down at room temperature. Then, the catalyst is stored inside the desiccator to avoid moisture in the catalyst.

2.3 In Situ Transesterification

The reactive extraction was carried out using the first parameter which was the effect of amount of catalyst. The amount of catalyst used was 2, 4 and 6 wt% for 3 hours. The fixed conditions used during the process was temperature (60°C), solid to methanol ratio (1: 10) and agitation speed at 350 rpm. Then, the second extraction was carried out by using different solid to methanol ratio (1:6 – 1:12) for 3 hours. The fixed conditions are temperature (60 °C), the amount of catalyst used based on the first reaction and agitation speed (350 rpm). The last reactive extraction was accomplished by using different temperature 50, 55 and 60 °C for 3 hours. The fixed conditions for this experiment were the amount of catalyst which was based on 1st reaction, the solid to methanol ratio based on 2nd reaction, and the agitation speed at 350 rpm.

3. Results and Discussion

3.1 Effect of Amount of Catalyst

The reactive extraction process was conducted by using amount of catalyst 2, 4, 6 wt. %. The fixed parameters were the solid to methanol ratio, temperature and mixing speed which were at 1:10, 60 °C and 350 rpm respectively. Figure 1 shows the result of biodiesel yield over time for different amount of catalysts. The biodiesel yield increase as the amount of catalysts increase especially at the first 30 minutes of reaction time. At 180 minutes of reactive extraction using 2, 4, 6 wt.% catalyst shows 26% ,31% and 47% of biodiesel yield respectively.

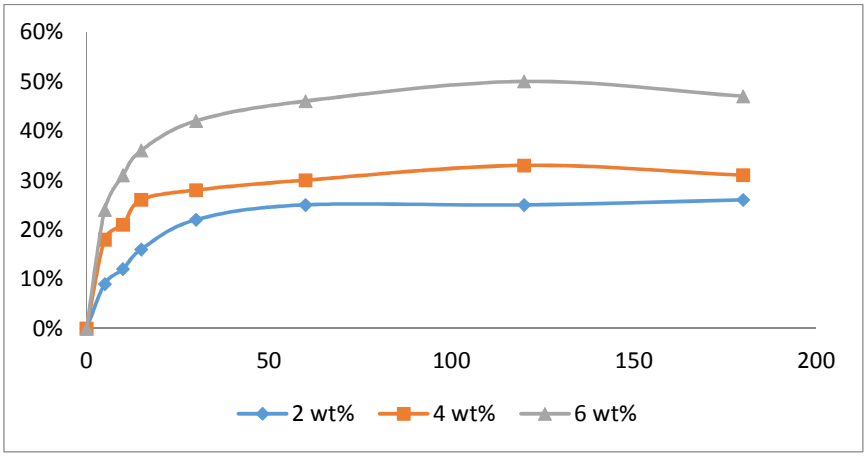

Fig. 1. Biodiesel yield vs time using different concentration of catalysts (2, 4, 6 wt.%)

According to Gashaw (2015), the yield of FAME increase with increasing amount of catalyst due to availability of more active sites by additions of more amount of catalyst in the transesterification process [12]. An estimate of the order of magnitude of the reaction time scale of a system is a definition of characteristic time. According to the graph, characteristic period can be observed when it reaches 20-30% of biodiesel yield right after the fast transesterification begin. For reaction containing 6 wt.% of catalyst, the characteristic time is 5 minutes, for 4 wt.% catalyst about 15 minutes, and 60 minutes for 2 wt% of catalyst loading.

According to previous studies by Birla et al., (2011), the yield of methyl ester increased steadily and then become constant at the catalyst amount of 3.0-3.5% with the increasing amount of catalyst [13]. The higher the catalyst loads, the conversion of triglycerides increases. The higher the concentration of catalyst, the longer time is needed to reach equilibrium in biodiesel conversion. The biodiesel production is in high amount although longer reaction time needed. The biodiesel yield that is accomplished the standard biodiesel is generally 95 % [14]. In comparison with the results obtained in the Fig. 1, the highest biodiesel yield was only 47 % which did not reach the standard.

3.2 Effect of Solid to Methanol Ratio

Based on results shown in figure 2, the biodiesel conversion gradually increased from 24% to 35% when solid to methanol ratio 1:8 and 1:10 are used. At solid to methanol ratio 1:12 the conversion decreased to 31% as it had no significant effect on the conversion of solid coconut waste into biodiesel. According to Asri *et al*., [15], when high excess of methanol consumed, the higher energy needed to recover the methanol and eventually will increase the production cost of biodiesel. Thus, it is not recommended. In this study, the optimum ratio of solid to methanol was 1:10. Transesterification is an equilibrium reaction. To shift the reaction forward, a large excess of alcohol is needed as it can reverse the reaction backward which is not favorable.

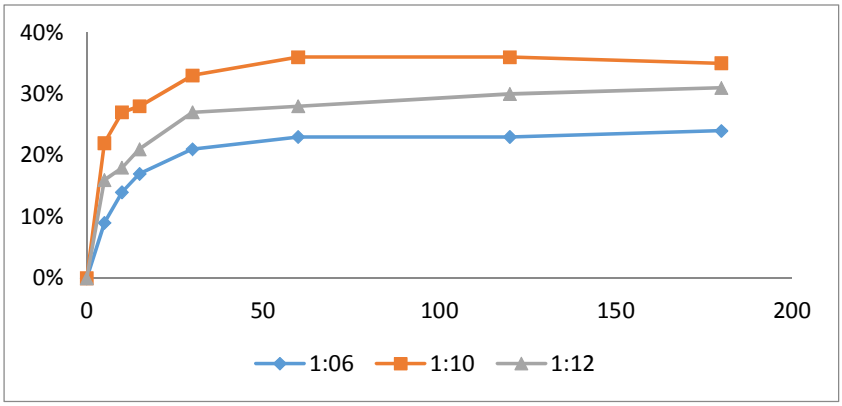

Fig. 2. Biodiesel yield over time at different solid to methanol ratio (1:6, 1:10, 1:12)

3.3 Effect of Temperature

Figure 3 presents the reactive extraction process which was conducted at various temperatures ranging from 50-60 °C. The result shows that the biodiesel yield increase as the temperature increase. Biodiesel yield at temperature 50 °C, 55°C and 60 °C were 30%, 34% and 38% respectively. The highest yield recorded at temperature 60 °C. Temperature becomes the leading factor influencing the rate of transesterification as the system becomes a kinetically controlled process.

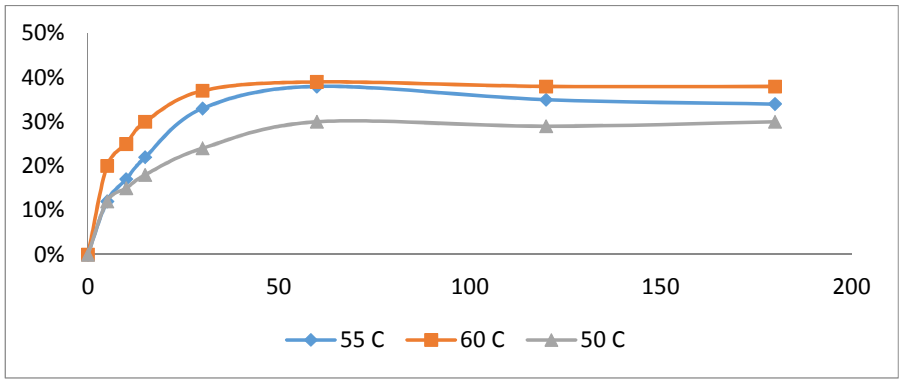

Fig. 3. Biodiesel yield as a function of time at different temperature (50,55,60 °C)

4. Conclusion

In this study, $CaO/Al_2(SO_4)_3$ was successfully produced fromegg shell and coconut waste. The solid coconut waste transesterification which were conducted at different amount of catalysts show that the biodiesel conversion increases with the increasing amount of catalyst which are 26%, 31% and 47% respectively. The optimum amount of catalyst, concentration of solid to methanol, and temperature needed to achieve highest yield of biodiesel, of 47 wt% was 6 wt.%, 1:10 and 60 °C.

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