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Pretreatment and Bentonite-based Catalyzed Conversion of Palm-rubber Seed Oil Blends to Biodiesel

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Abstract

Pretreatment of pre-blended palm and rubber seed oil (50:50) was studied. A parametric study to determine the effect of alcohol-to-oil ratio, catalyst loading and reaction temperature on free fatty acid (FFA) content was also conducted. Interestingly, the FFA percentage of pre-blended feedstock has been reduced significantly from 20% to below 2%. The optimum value for the reduction of FFA was found to be 1.5 wt. % catalyst, alcohol-to-oil ratio 6:1, 62ºC reaction temperature at constant stirring speed (400 rpm) and reaction time 1.5 hours. NaOH/bentonite was also investigated and characterized as a solid heterogeneous catalyst for transesterification. The characterization was conducted by FTIR and XRD analysis. The catalyst showed good results by producing 92 wt% fatty acid methyl esters at reaction temperature of 62°C and reaction time of 3 hours.

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Keywords: Pre-treatment; Impregnation; Transesterification; Biodiesel

1. Introduction

Petroleum consumption has been increased during the last 25 years because of higher living standards and increased transportation. To avoid any distortion the world is focusing on the alternative and renewable resources. Recently, a lot concern has been aroused because of increased oil prices and reduction in fossil fuel resources [1]. Due to this, renewable energy resources have taken much attention these days as a fuel replacing fossil fuels.

The demand of energy and pollution issues due to transportation in developed countries signals the need to search for renewable energy resources to replace fossil fuels having lesser effects on environment [2]. Biodiesel as a first generation biofuel consisting of alkyl esters is the most attractive fuel now a days because of its biodegradability, better lubricity and low emission of SO_X and NO_X [3]. The use of biodiesel not only will reduce the use of fossil fuels but also helps to reduce the emission level of pollutants. Pure biodiesel (B100) used in place of petroleum derived diesel reduced CO_2 emission by 80 % [4].

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Currently, five biodiesel plants are fully operational in Malaysia and to raise the production up to 3 million tons annually five more plants have been approved. Malaysia mostly produces biodiesel from palm oil as it is the second largest producer of palm oil in the world after Indonesia [5]. If palm oil is consumed in the same way it will definitely disturb food resources. Non-edible oils are found to be a promising alternative and have numerous advantages over edible ones. Non edible oils have many benefits such as economical, reducing expenditure on imports and fuel versus food controversy. Rubber seed oil (non-edible) is another abundant plantation in Malaysia cover more than 1.2 million ha all over the country [6] but the only drawback is its high acid value. Pre-treatment of the oil has been done in many studies in order to reduce the FFA % below 2% by esterification reaction, converting FFA to fatty acid methyl esters to avoid soap formation and for the production of good quality biodiesel [7]. Commonly NaOH and KOH are being used as homogeneous alkali catalysts for biodiesel production because of their low cost easy availability and their high catalytic performance under moderate conditions. Therefore most of the researchers studied two-step process by first reducing the FFA content up to the desired level by esterifying the oil with acid catalyst and then used the homogeneous alkali catalyst for transesterification [8, 9].

Homogeneous acid catalysts such as Sulfuric acid, hydrochloric, phosphoric and organic sulfonic acids can be used as a catalyst for biodiesel production. Besides no soap formation, rate of reaction has been very low. Acid catalyzed transesterification reaction is reported as 4000 times slower than that of alkali transesterification reaction [10, 11]. The acid catalyzed reaction takes 2-48 hours and requires temperature above 373K [12].

Recently, many researchers were performing experimentations with the aim to find solutions of the problems encountered by using homogeneous catalyst for transesterification reaction. As a result of exploration many of the solid catalysts have been explored with better catalytic performances. Yan and Salley [13] studied simultaneous esterification and transesterification in a single step and 96% conversion is achieved in 3 hours by using $ZnO-La_2O_3$ as a solid heterogeneous catalyst. Although this process is good with respect to conversion of the reactants but not so economical because of the expensiveness of Lanthanum is a rare earth metal. Currently oxides of alkali or oxides of alkaline earth metal supported over large surface area are used in producing biodiesel. Heterogeneous catalysts are advantageous as compared to homogeneous catalyst such as; easy catalyst recovery, simple product purification, less purification cost, regeneration, easy recovery of glycerol, less energy and water consumption. Besides this mostly higher yields have been observed while using solid alkaline catalysts [9].

Clay materials are pervasive in nature as well as heterogeneous in its composition, particle size and also serve as good adsorbents [14, 15] . Different materials have been used previously as solid heterogeneous catalysts such as La_2O_3/ZrO_2, CaO, WO_3/ZrO_2 [16-18] but the use of clay materials as solid catalyst is rarely been found. In the present study the pre-treatment of pre-blended (50:50) palm and rubber seed oil has been done using sulfuric acid as acid catalyst to reduce %FFA from 20% to less than 2% and studied the influence of operating parameters such as; alcohol to oil ratio, catalyst loading and reaction temperature. Secondly bentonite has been investigated as a solid heterogeneous catalyst for transestesterification reaction to produce biodiesel. Rapeseed oil has been used a model feed stock to check the catalytic performance and feasibility of using bentonite as a solid basic catalyst for the transesterification of pretreated palm and rubber seed oil blend(50:50) and also as an adsorbent in the decolourization of dark coloured biodiesel.

2. Materials and methods

2.1 Materials

The palm oil was purchased from Malaysia and rubber seed oil was imported from Vietnam. Pure rapeseed oil, bentonite, methanol and sodium hydroxide were purchased from Wako Pure Chemical Industries, Ltd. (Tokyo, Japan)

2.2 Experimental setup for acid esterification

Acid esterification is the step that reduces the FFA % of the oil to below 2% using acid catalyst. All the experimental runs were performed by using a 250 ml three neck round bottom flask with a condenser attached to minimize the alcohol losses. The whole equipment assembly was placed on a heating plate at a constant stirring speed of 400 rpm for 1.5 hour [8]. A known amount of catalyst was added to the known volume of methanol. In order to monitor the reaction temperature, a thermometer is inserted in one of the necks of the round bottom flask. When the esterification reaction was completed, the mixture was poured in a separating funnel and the separation was done under the action of gravity. After 2 to 3 hours, the upper layer with excess methanol, glycerol and catalyst was removed and the bottom layer of the desired product was washed several times with warm de-ionized water until the PH was neutral. After the reaction, separation and washing of the product, the acid value was calculated by using AOCS official method (Cd 3d-63) [19].

2.3 Catalyst preparation for transesterification reaction

Bentonite was activated by heating it at 500 °C in a muffle furnace and then impregnated with sodium hydroxide. The impregnation was conducted at 60 °C for 12 hours under continuous stirring with 1:20 bentonite to sodium hydroxide ratio. After that the slurry was dried at 110 °C for 12 hours and then calcined at 500 °C in a muffle furnace for 5 hours [20].

2.4 Catalyst characterization

Raw bentonite and impregnated bentonite were analyzed by X-ray diffraction method (XRD). Rigaku Miniflex600 Goniometer recorded the XRD patterns of bentonite with the use of Cu Kα radiations at 0.01° step size. The qualitative analysis of both raw and impregnated bentonite were conducted by FTIR method on Jasco FTIR-4100 instrument using KBr technique

2.4 Transesterification using rapeseed oil as feedstock

Transesterification of rapeseed oil was conducted in a three neck round bottom flask with condenser at the top under continuous stirring. The controlled water bath heater was used to maintain the reaction temperature at 62 °C. Rapeseed oil was added into the reactor under continuous stirring of 500 rpm. Methanol to oil ratio used in this study was 6:1 with reaction time 1-6 hours. The tranesterification reaction was carried out using 3 wt. %, 5 wt. % and 10 wt. % of catalyst. After the completion of the reaction, the product was allowed to settle over night to get two separate layers of biodiesel and glycerol.

2.5 Determination of methyl ester yield

Fatty acid methyl esters (FAME) produced by transesterification of rapeseed oil using bentonite as catalyst were analyzed by using Shimadzu GC-14B with DB-5 Wax capillary column of 30m length and 0.25mm internal diameter, J&W Scientific and FID (flame ionization detector). The column and detection temperatures were 240 °C and 310 °C respectively. Dimethyl naphthalene was used as an internal standard and was injected in the column by mixing with hexane and 50 µL volume of sample. Peaks of methyl esters were identified by comparing them with reference standard.

3. Results and discussion

3.1 Acid catalyzed pre-treatment process

3.1.1 Effect of catalyst dosage

The most commonly used acid catalyst for the pre-treatment process is sulfuric acid (H_2SO_4), because of its easy availability and low cost. The results showed the effectiveness of catalyst. At 0.5 wt % of the catalyst lower reduction in FFA % was observed and it was still higher than 2%. The FFA percentage decreased from 20% to less than 2 from the dosage 1% to 2.5 % as shown in Fig 1(a). After 2.5 %, there is no such reduction observed in the FFA content. The increased catalyst amount (above 2%) darkens the colour of oil. The optimum dosage was found to be 1 % for esterification of pre-blended palm and rubber seed oil.

3.1.2 Effect of reaction temperature

In most of the previous studies the reaction time was maintained between 45 ºC-65 ºC by many researchers [21, 22]. The effect of temperature on the reduction of free fatty acid content has been shown in Fig 1(b). In the current study, the optimum reaction temperature was found to be 62 ºC, reduced FFA % below 2 %. On increasing the temperature above 65 ºC, again increase in FFA content was observed due to alcohol loses.

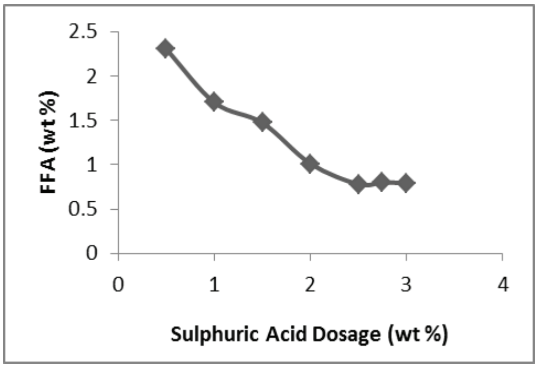

Fig 1(a). Effect of catalyst amount on FFA content

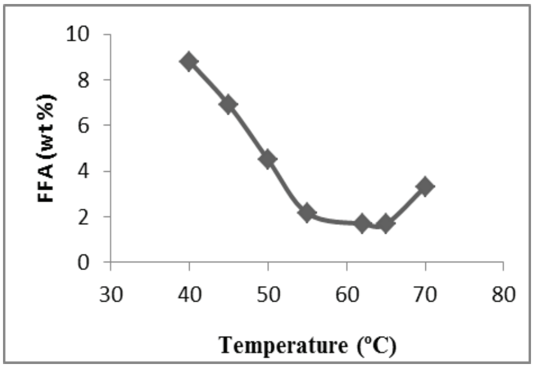

Fig 1(b). Effect of reaction temperature on FFA content

3.1.3 Effect of alcohol-to- oil ratio

Molar ratio is another very important factor that effects the conversion of FFA to fatty acid methyl esters. It is the ratio of number of moles of alcohol to number of moles of oil. Theoretically for esterification reaction, for each mole of oil three moles of alcohol are required. In practice, as esterification is an equilibrium limiting reaction, in order to shift the reaction equilibrium to the product side, alcohol to oil ratio should be higher than the stoichiometric value. In the present study, the molar ratio was varied from 3:1 to 10:1. Fig 2 describes the effect of molar ratio in the reduction of FFA % of oil. The maximum reduction in FFA % was observed near 6:1, on increasing further, no prominent change was observed. For this study, 6:1 was selected as the optimum value for alcohol to oil ratio.

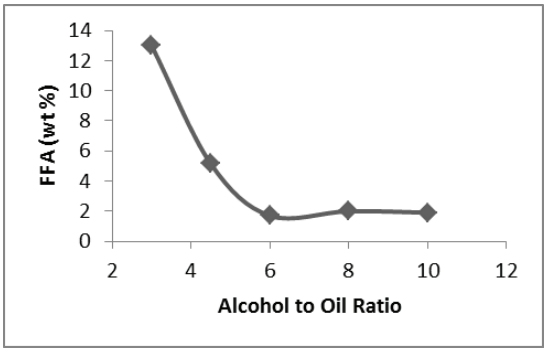

Fig 2. Effect of alcohol to oil ratio on FFA content

3.2 XRD measurement and FTIR analysis of bentonite and NaOH/bentonite

The XRD results of raw bentonite and NaOH/bentonite (1:20) are shown in Fig 3(a) (b). Catalyst crystallinity increased on NaOH loading on bentonite. The XRD pattern of NaOH/bentonite (1:20) was very similar to the raw bentonite but a new phase of Na_2O appeared on the pattern. Na_2O formed during calcination of catalyst as it appeared on XRD pattern. The presence of Na_2O phase was indicated by the reflections around 2Θ= 34°, 37°, 47° and 51°.

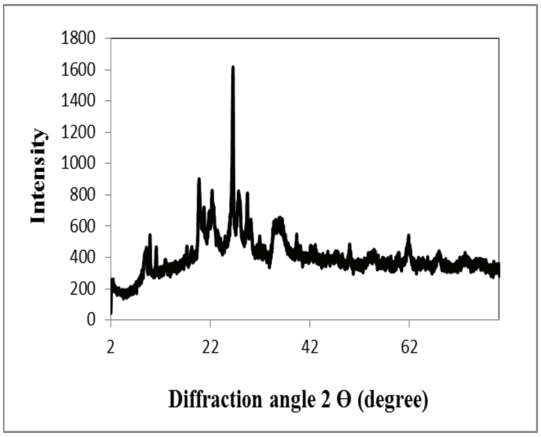

Fig 3(a). XRD pattern for raw bentonite

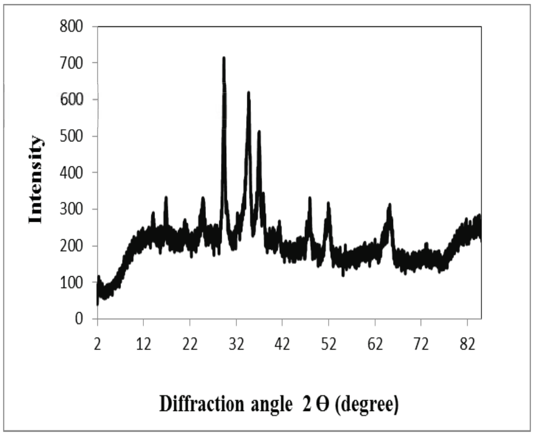

Fig 3(b). XRD pattern for NaOH/bentonite

The FTIR spectrum of bentonite shown in Fig 4, indicates the presence of different functional groups such as Al (Mg)-O-H stretching at 3611 cm^{-1}, H-O-H stretching at 3386 cm^{-1}, H-O-H bending at 1622 cm^{-1} and Si-O-Si stretching at 1056 cm^{-1}. The addition of NaOH prominently affected the structure of bentonite (as shown in Fig 4) by changing the -intensity of stretching group Al(Mg)-O-H indicated the new functional group Al-O-Na in the catalyst structure [20].

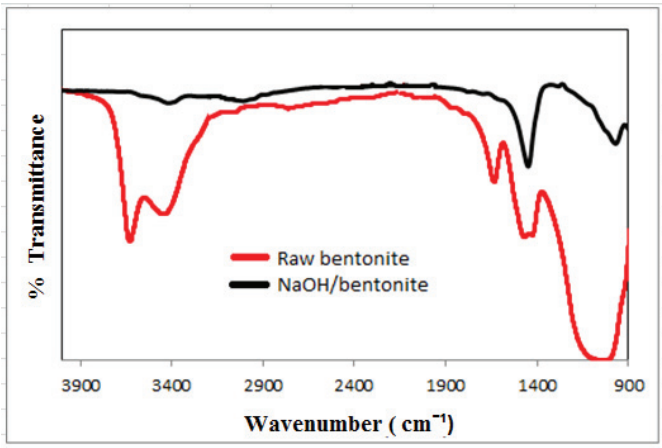

Fig 4. FTIR spectra of bentionite and NaOH/ bentionite

3.3 Transesterification using NaOH/Bentonite as catalyst

3.3.1 Effect of impregnated bentonite catalyst loading on biodiesel yield

The catalytic performance was investigated from fatty acid methyl ester yield. The catalytic amounts used of transesterification of rapeseed oil were 3, 5 and 10 wt. %, 6:1 methanol to oil ratio, 62°C reaction temperature and 6 hours reaction time. Fig 4 clearly indicated the increase in fatty acid methyl ester content on increasing the weight percentage of catalyst. At 3 wt. % of catalyst, 94% yield is observed and it increased to 97% and 99% for 5 wt. % and 10 wt. %, respectively as shown in Fig 5.

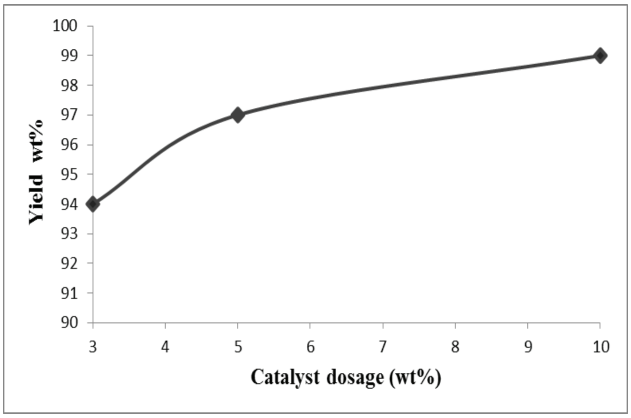

Fig 5. Effect of catalyst amount on biodiesel yield

3.3.2 Effect of reaction time on biodiesel yield

The effect of reaction time on biodiesel yield has been shown in Fig 6. In this study, transesterification reaction was carried out for 1-6 hours at 62 °C, 3 wt. % of catalyst and 6:1 alcohol-to-oil ratio. The optimum reaction time was found to be 3 hours, after that no prominent change was observed in biodiesel yield. After one hour, 70 % yield is observed which increased up to 92 % after 3 hours and reached 94% after 6 hours. NaOH/bentonite catalyst showed promising results for fatty acid methyl esters yield.

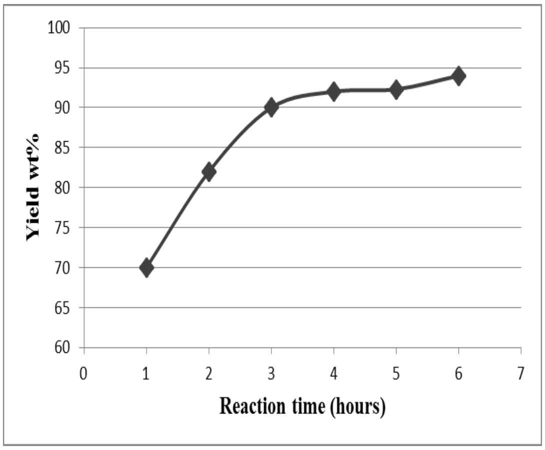

Fig 6. Effect of reaction time on biodiesel yield

4. Conclusion

It was found that pre-blended palm and rubber seed oil could be used as a viable feedstock for biodiesel production after pre-treatment. The optimum conditions for acid catalyzed pre-treatment were obtained by using sulfuric acid as an acid catalyst at 1 wt. % , alcohol-to-oil ratio of 6:1 and reaction temperature of 62 ºC. The optimum conditions were validated and FFA % was reduced from 20% to less than 2 %. NaOH/bentonite was also investigated as a solid heterogeneous catalyst for transesterification using rapeseed oil as a model feedstock. The catalyst showed promising results by giving 92 wt. % yield at 62 °C and reaction time of 3 hours. These results revealed that NaOH/bentonite catalyst is feasible to use for the transestertification of pre-blended palm and rubber seed oil after pretreatment. The future task will be the study of decolourization of biodiesel using bentonite catalyst and development of heterogeneous catalyst viable for both esterification and transesterification simultaneously.

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