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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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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].

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