Biodiesel Production Catalysed by Magnetic Palm Kernel Shell-Potassium Hydroxide

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Abstract. Biodiesel was prepared by transesterification process using heterogeneous catalyst has received a lot of interest lately as a sustainable source of biofuel. Hence, there is a need to study a generalized reaction kinetic model that can be used for all the reactions involved in biodiesel production. This study produces biodiesel by transesterifying palm oil using magnetic palm kernel shell-potassium hydroxide. The catalyst recorded a BET surface area of 47.72 m^2/g. The maximum biodiesel yield, 95.78%, was obtained when reaction temperature and time were 55°C and 2 hours, respectively.

1. Introduction

Fatty acid methyl ester (FAME), a biofuel substitute for petroleum diesel, is biodiesel. Because it can be produced from abundantly available vegetable or animal resources, biodiesel is preferred over petroleum-based diesel. Biodiesel's emissions due to combustion carry properties of being biodegradable, non-toxic and sulphur and aromatics free. Additionally, it is safer to use and has superior lubricity versus fossil fuel [1]. Commonly, the homogeneous catalysed transesterification of alcohol and triglycerides to produce biodiesel has increased catalytic activity. Examples of this catalyst are potassium hydroxide (KOH), and CH_3CH_2ONa [2]. However, these catalysts have portrayed some drawbacks like their properties of non-recyclability and an unavoidable production of toxic water [3]. The quantity and quality of the biodiesel can both be improved by the heterogeneous catalyst. The downstream separation stages related to glycerol's by-product can be further simplified. The likelihood of reusability for heterogeneous catalysts is high, which helps with the process' economics [4]. Several catalyst backings have been researched, for example, CaO, MgO, Al_2O_3, and so on [5]. However, if green catalysts are employed, biodiesel production may be improved to a more cost-effective and environmentally beneficial energy source. Normally, green catalyst, also known as biomass-derived carbon material is famous for being naturally porous and owns a high surface area prior to the minor altercation. This being stated, it can be effectively utilized for transesterification [6]. One example of an excellent feedstock for green catalyst is oil palm's palm kernel shell (PKS). PKS derived activated carbon catalyst has been reported to have excellent catalytic activity and physicochemical properties [7, 8]. Furthermore, the utilization of waste oil palm biomass such as PKS will help the environment by reducing the waste mass going into landfill and producing a profitable by product at the same time [9, 10].

The cost of raw materials used in producing biodiesel has become the key cause of high prices in the production process. An ideal raw material must always be readily available, cost less and be permanent. The easy access to palm oil and the ever-stable supply supports its choice to be the raw material. Single step transesterification process is favourable to synthesize the palm oil to methyl ester. It needs less reaction time, temperature, and pressure, so all these factors will conclude in lower price costing of production [11]. This study's goal is to use transesterification reaction to turn palm oil into biodiesel with the help of a heterogeneous catalyst made of activated carbon and palm kernel shell (ACM-PKS) with potassium hydroxide as catalytic functional species. Methanol was used as the alcohol solvent component as its price is lower than other alcohol choices.

Biodiesel has transitioned from the scale of laboratories into commercial production. For extensive biodiesel production in industries, high oil conversion in brief transesterification times is crucial. Mass transfer, reaction kinetics, and component solubility all have an effect on the total reaction rate [12]. It is important to research the chemical processes used in the manufacture of biodiesel. In this work, the effects of transesterification and the basic heterogeneous catalyst ACM-PKS on the reaction temperature and period were examined.

2. Materials and Method

2.1. Materials

PKS biochar was chosen as the carbon precursor for synthesising solid alkaline catalysts. This PKS was obtained from Sarawak Oil Palms Berhad. Chemicals: Ferric chloride, $FeCl_3 \cdot 6H_2O$ (Merck, 95-97%), potassium hydroxide, KOH (Merck, 0.01M), and methanol, CH_3OH (Merck, $\geq$99.5%) were purchased. Buruh refined cooking oil (pure palm olein) was procured as the raw oil feedstock.

2.2. Catalyst Preparation

To eliminate any foreign materials, such as dust and grime, tap water was used to rinse raw PKS. The raw PKS was then oven-dried (400L, ED400, Binder) for 24 h at 110 °C temperature. Mortar and pestle were utilized to ground the washed raw PKS at ambient condition to obtain a powder state. 50 g of PKS biomass was mixed with 500 mL of distilled water. 18 g of anhydrous ferric chloride was mixed with 1300 mL distilled water to formulate 0.085M ferric chloride solution ($FeCl_3 \cdot 6H_2O$). These two solutions were combined. The mixture was heated in a 2 L beaker between 60 and 70 °C temperature, vigorously stirred for 24 h with a magnetic stirrer (C-Mag HS 7, IKA) and oven-dried for another 24 h at temperature of 110 °C. 2M KOH solution was applied to activated carbon for 24 h at 25 °C with an orbital shaker (KS501, IKA). The mixture was oven-dried at 110 °C temperature overnight. The dried sample was put through pyrolysis for 5 h at 500 °C before being dried in an oven at 110 °C for 24 h. The resulting ACM-PKS (0.085M $FeCl_3$ and 2M KOH) catalyst was stored in a sealed container. The obtained ACM-PKS catalysts were then further analysed to identify their material characterization. The catalyst's porosity and Brunauer-Emmett-Teller (BET) surface area were measured using a gas sorption analyzer (TriStar II Plus), while the catalyst's magnetic characteristics at room temperature were evaluated using a vibrating-sample magnetometer (VSM; Lakeshore-7400).

2.3. Biodiesel Production

1.305 g or 7.5 wt% of ACM-PKS catalyst and 5 mL of methanol were mixed in a 50 mL Erlenmeyer flask with a screw cap. 20 mL or 17.4 g of palm olein refined cooking oil and the methanol-catalyst mixture were heated for catalyst activation at set temperature for 30 min. The set oil to methanol molar ratio was 1:6. The cooking oil was mixed into the methanol-catalyst mixture for transesterification reaction initiation. The transesterification was carried out at set temperature (55 ºC, 65 ºC and 75 ºC) and at a cyclic rate of 200 rpm inside a shaking incubator (LABNET-USA). The reaction duration was set to range from 60 min. to 240 min. with 30 min. interval. The heating and agitation were halted after this duration and the product was allowed to form two distinct layers. Methyl ester phase at the top and the denser phase of glycerol at the bottom. The biodiesel phase was centrifuged (Universal 320R, Hettich) and further washed multiple times with warm deionized water until it became clear. Lastly, the calculation for the yield was carried out from the weighed biodiesel through the following equation [13]:

$$\text{Yield (\%)} = \frac{\text{Weight of biodiesel (g)}}{\text{Weight of oil (g)}} \times 100 \tag{1}$$

3. Results and Discussion

3.1. Catalyst Characterization

3.1.1. BET. To investigate the surface area of constructed ACM-PKS, single point nitrogen gas adsorption characterisation was carried out. The BET surface area of raw PKS and ACM-PKS are shown in Table 1. Raw-PKS recorded the lowest surface area, which is 1.79 m^2/g. This is caused by the thick raw-PKS structure, which is devoid of pores on the surface of the Raw-PKS and contains lignin, cellulose, and hemicellulose. The surface area of ACM-PKS increases by 45.93 m^2/g upon activation. This demonstrates that KOH is an effective activating agent. [14]. The primary cause of the activated carbon's increased surface area is gasification. The creation of pores on ACM-PKS structure is due to the gasification's partial or complete elimination of volatile substances. [15].

Table 1. Surface Area with respect to different concentration of KOH.

Sample	**Concentration of potassium hydroxide (M)**	**BET Surface Area (m^2/g)**	**Total pore volume (cm^3/g)**	**Average pore size (nm)**
RAW PKS [15]	0	1.79	0.01	-
ACM-PKS	6	47.72	0.03	22.37

3.1.2. VSM. A VSM was used to evaluate the catalyst's magnetic strength. According to studies, activated carbon gains magnetic qualities from the additional magnetic components during the magnetization process, which also increases the adsorption capability [16]. The magnetization (Ms) value of the catalyst is 2.5331 emu/g as shown in Figure 1. Even though the magnetization values are not high, it is still considered satisfactory. It is predicted to result in fitting magnetic responsive property to the magnetic field. However, the magnetism of the catalyst might further reduce after the transesterification process due to the same problem. ACM-PKS displayed the characteristic superparamagnetic behaviour, as seen by the hysteresis loop. According to a prior study, superparamagnetic behaviour is a characteristic that magnetic materials typically exhibit after the application of an external magnetic force. This magnetic material's particles display magnetism [17]. It also explains why ACM-PKS has a high Ms [15].

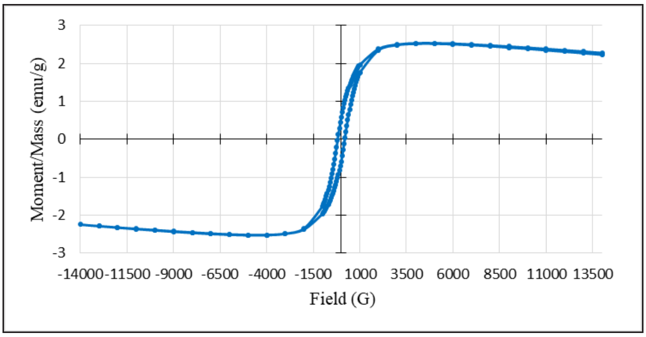

Figure 1. Magnetization hysteresis loop for ACM-PKS catalyst (0.085M $FeCl_3$ + 2M KOH PKS).

3.2. Biodiesel Yield of Palm Oil Via ACM-PKS Catalysed Transesterification

Figure 2 shows the biodiesel yield that was attained following the transesterification procedure employing ACM-PKS as a catalyst for multiple experimental runs under variable temperature, time, and methanol-to-oil ratio circumstances. A temperature of 75 °C and a reaction time of 4 h produced the lowest biodiesel production of 70.12%, while a reaction temperature and reaction time of 55 °C and 2 h respectively, produced the highest yield of 95.78%.

The mild reaction variables that were used to get the high biodiesel yield were sufficient to produce biodiesel. Due to methanol evaporation and the reversibility nature of transesterification reaction, higher reaction variables resulted in a decrease in biodiesel production. When transesterification of palm oil catalysed by pyrolyzed PKS was investigated, Baroutian et al. [18] found a similar outcome. A production of 98.03% biodiesel was attained. Additionally, it showed that a reaction temperature of 64.1 °C was sufficient for the whole transesterification of palm oil in an average reaction time of 1 h. The transesterification processes were also successful at 6:1 methanol-to-oil molar ratios. Reaction times longer than 2 h indicated lower biodiesel production. This is due to the transesterification's unbalanced (reversibility) character on both the reaction and product sides. Additionally, a larger methanol-to-oil molar ratio could result in less triglyceride molecule interaction with the catalyst's active sites, which would diminish catalytic activity [19]. This increased the generation of glycerol and encouraged backward processes, which decreased the yield of biodiesel. The changing biodiesel yield numbers provide evidence that the reaction parameters for palm oil transesterification have a significant impact on the biodiesel production. The impact of reaction parameters on the synthesis of biodiesel employing the catalyst ACM-PKS is depicted in Figure 2.

3.2.1. Reaction Temperature. The percentage of biodiesel conversion relative to the reaction temperature is depicted in Figure 2. At hree different temperatures with a reaction time of between 60 and 240 min., the experiment was carried out. Each point in Figure 2 verifies the average biodiesel % for all runs at the same temperature (55 °C, 65 °C, and 75 °C). The yield rate was slow at low temperatures and the proportion of biodiesel grew dramatically as the temperature rose. It was discovered that 55 °C produced the highest proportion of biodiesel from palm oil utilising the ACM-PKS catalyst. A further rise in temperature, however, resulted in a decline in the percentage of biodiesel since the reaction temperature is already greater than the boiling point of methanol under normal pressure settings. Because it is so close to both the maximum melting point of crude palm oil (55 °C) and the boiling point of methanol (64.6 °C), a reaction temperature of 55 °C is adequate. Additionally, a rise in reaction temperature speeds up the saponification of glycerides by the alkaline catalyst due to the high FFA level in oil.

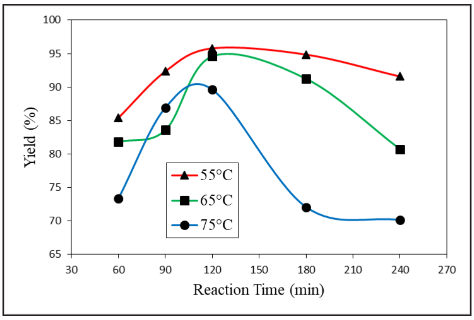

Figure 2. Effect of temperature on biodiesel yield using ACM-PKS as a catalyst (Molar ratio to methanol at 1:6, catalyst loading at 7.5wt% and stirring rate at 200rpm).

3.2.2. Reaction Time. Given how quickly the transesterification process occurs, response time is essential. Figure 2 illustrates the relationship between biodiesel production and reaction time that was researched. As can be seen, yield grows with time and, because the reaction is reversible, it virtually becomes constant after a certain reaction period. The yield for the ACM-PKS catalyst reaches 95.78% after 120 minutes of batch time at 55 °C, indicating that the transesterification reaction is relatively rapid. From reaction time of 120 to 240 min., the biodiesel yield drops by 4.20% for reaction temperature of 55 °C, 13.87% for reaction temperature of 65 °C, and 19.51% for reaction temperature of 75 °C. The transesterification rate of a certain feedstock is shown by the reaction time. The conversion of triglycerides was unaffected by extending the reaction time from 4 to 6 h, although the product yield was decreased. Since a longer reaction time accelerated the hydrolysis of biodiesel, transesterification reverse reaction, the yield was reduced.

4. Conclusion

PKS, a waste product from palm oil mill, was used to produce carbon support before being magnetized and impregnated with KOH to produce the magnetic solid base catalyst, ACM-PKS. More pores are forming on the surface of the ACM-PKS catalyst, as evidenced by the considerable increase in BET surface area to 47.72 m^2/g. Biodiesel production at a temperature and period of 55 °C and 2 h respectively, the highest biodiesel production of 95.78% was attained. Using 6:1 methanol-to-oil ratio, and a catalyst amount of 7.5 wt%, this scenario was accomplished. Due to its environmental friendliness and exceptional separation efficiency, the use of magnetic catalysts made from biomass has emerged as a possible alternative to the existing biodiesel catalyst trends. Costs associated with producing biodiesel can be implicitly decreased using magnetic biochar catalysts by lowering time and energy requirements. In order to fill the existing research gap, develop the biodiesel sector, and commercialise it in order to build a greener and more sustainable future, it is crucial to conduct ongoing research.

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