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Synthesis and Characterization of K_2O/ACT Catalyst for Biodiesel Production from Beef Fat Waste

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Abstract: The increasing use of petroleum as fuel has depleted fuel, so alternative fuels such as biodiesel are needed because they are environmentally friendly and come from vegetable and animal sources. Therefore, this article presents biodiesel production from beef fat using a K_2O/ACT heterogeneous base catalyst derived from egg shells. The Eggshell becomes a CaO catalyst after 3 hours of calcination at 900°C. The K2O/ACT catalyst was synthesized by impregnating CaO with KOH and characterized using XRD and BET. The K2O/ACT catalyst was compared to the CaO catalyst for transesterification activity under appropriate conditions (reaction temperature 65°C, catalyst loading 3% by weight, oil to methanol molar ratio 1:12, and reaction time 3 hours). The catalytic activity of the catalyst was determined to be 98.40% Fatty Acid Methyl Ester (FAME). The insertion of K_2O into the CaO catalyst increases the basicity characteristics, thereby increasing the catalytic activity of transesterification.

Keywords: Beef Tallow; Biodiesel; Impregnation; KOH/CaO Catalyst.

Introduction

Because people rely on petroleum as a fuel, it is one of Indonesia's most prominent nonrenewable natural resources [1]. Global energy demand increased by 45%, or 1.6% annually on average [2]. As a result, there is a demand for oil fuel replacements such as biodiesel [3][4]. Biodiesel is frequently used as a petroleum substitute since it does not necessitate adjustments to machinery or new equipment [5]. This does not always apply to bioethanol, typically mixed with gasoline [6].

Biodiesel is diesel engine fuel in the form of fatty acid methyl ester (FAME), produced by esterifying or transesterifying vegetable oil or animal fat [7]. Biodiesel manufacturing can minimize reliance on fossil fuels, is more environmentally benign, and can be derived from animals, plants, or agricultural waste [8]. One of the raw ingredients used to make biodiesel is animal fat, such as beef grease, which is inexpensive and easy to get and may be utilized to produce liquid fuel [9]. However, its potential has not been fully realized. Beef fat contains the most methyl ester, at 89.91% [10], followed by chicken fat at 88.12% [11] and hog fat at roughly 84.45% [12].

A catalyst is required in biodiesel production because it provides another reaction mechanism with lower activation energy, allowing the reaction to achieve equilibrium faster and without undergoing chemical changes after the response [13]. The process can be sped up at the same temperature by lowering the activation energy [14]. Eggshell ash (ACT) was chosen as a catalyst material in the production of biodiesel because it includes calcium carbonate [15] and is relatively inexpensive because it can be easily obtained from natural materials such as eggshell waste [16]. $CaCO_3$ is the major component of egg shells, which calcination can transform into CaO [17]. As a result, it is believed that egg shells can be used as a source of high-purity CaO that can operate as a catalyst. The CaO catalyst is heterogeneous and basic [18]. Homogeneous catalysts such as acids (H2SO4) and bases (NaOH or KOH solutions) are frequently used in biodiesel manufacture.

However, there is a drawback to using this catalyst: the separation of the catalyst from the product is difficult. Furthermore, homogeneous catalysts can interact with free fatty acids (ALB) to form soap, which complicates the purification process, reduces biodiesel output, and increases catalyst consumption in the methanol reaction [19]. This study focuses on producing biodiesel from beef tallows utilizing a K_2O/ACT catalyst and researching biodiesel manufacturing from beef tallows.

Research Methods

Materials and Tools

Eggshells come from MSMEs in the Sukodono area, Sidoarjo. Beef fat comes from food production in the Tegalsari area, Surabaya. The chemicals used for experiments and analysis are solid KOH, 96% H_2SO_4, 99% methanol, and phenolphthalein indicator. The tools used are a 500 ml three-neck flask, thermometer, condenser, magnetic stirrer, stirrer, oven, baking pan, 250 ml Erlenmeyer flask, 500 ml beaker glass, 1000 ml measuring flask, separatory funnel, bucket, hose, water pump, flask measuring, dropper pipette, 50 ml measuring cup and analytical balance.

Catalysts Preparation

Impregnation uses a CaO: KOH ratio of 1:33, namely 5.6 grams of calcined ACT dissolved in 100 mL of

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KOH solution weighing 0.169 grams, then stirred by heating the mixture at 85°C while stirring until dry. The impregnated catalyst was then dried in an oven at 105 °C for 24 hours and then calcined at 500 °C for 5 hours [17].

Catalysts Characterization

The catalyst was characterized based on powder X-ray Diffraction (XRD) and Brunauer-Emmer-Teller (BET) surface area.

XRD analysis uses a PANalytical X'pert PRO Analytical diffractometer with an XRD pattern with 2θ measurements between 10° to 60° to produce a diffraction pattern from the powder crystal sample at ambient temperature. XRD pattern analysis was identified using the Powder Diffraction File (JCPDS) database [20].

The catalyst's specific surface area and pore size distribution were determined from BET analysis using Quantachrome TouchWin v1.22, SAA Full Isotherm 20pts with a temperature of 300 °C and a degassing time of 6 hours. For analysis of catalyst surface area and pore size distribution, the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods were used, respectively [21].

Catalysts Testing

The K_2O/ACT catalyst activity test was carried out on biodiesel production made from beef fat. The synthesized catalyst was put into a three-neck flask with added oil: methanol 1:12, homogenized at 65°C for 2 hours. After that, the mixture was transferred into a separating funnel and allowed to stand until two layers formed. The top layer was separated and washed with water at 80°C. The upper and lower layers formed were separated, and the remaining water content in the upper layer was evaporated at 105°C for 30 minutes [22]. The resulting FAME biodiesel was characterized and identified using GC-MS.

Results and Discussion

XRD Characterization

XRD results tested on CaO and K_2O/ACT samples each is shown in Figure 1. The CaO diphragtogram shows 2θ = 37.2360° ; 37.3505° ; 53.7358° and 32.0570°. This XRD result is similar to the CaO XRD pattern reported by (Mohadi et al., 2016) with high intensity at 2θ = 33.9821°; 32.1906°; 37.5410° so that the sample is identified as a chemical compound [23]. In the K_2O/ACT catalyst, K_2O appears at 2θ 33.9821°; 17.9750°; 50.8009°; 37.3471; 28.6979° and 46.9958°. by the research results of Hossain et al., (2021), namely KOH impregnation of eggshell ash produces a peak intensity of 2θ = 32.14º; 37.30º; 53, 82º; 64.18º; and 67.34º [24]. And in (JCPDS File No. 47-1701) the k2O peak appears at 28.98°. The presence of the K_2O compound indicates the success of the K_2O/ACT catalyst impregnation process.

Surface area

The surface area of the catalyst is an essential requirement because it determines the number of active sites in the catalyst, which is related to its activity [25]. The surface area of the catalyst was determined in this study using the nitrogen adsorption-desorption method, which estimates the amount of gas adsorbed on the surface of the material described to determine the active surface area of the catalyst. Impregnated with KOH with the help of CAO, carried out on a NovaWin Quantochrome apparatus with an immersion temperature of 300°C. Table 1 shows the results of BET characterization.

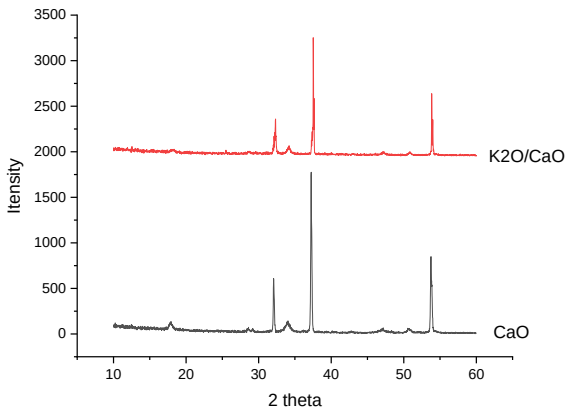

Figure 1. Peak XRD

Table 1. Results of surface and pore analysis of synthesized samples

Sample	Surface area specific (m^2/g)	Average pore diameter (Å)	Total Pore Volume (cc/g)
CaO	0.959	17.8269	8.544×10^{-3}
K_2O/ACT	10.487	7.95623	4.171×10^{-2}

This shows the presence of K_2O compounds in K_2O/ACT with a significant increase in the surface area of the catalyst. The rise in catalyst surface area may be due to increased base active sites and increased catalyst activity in the transesterification process, as Istadi reported [26].

Catalyst Activity in Biodiesel Production

The transesterification stage aims to convert ingredients such as triglycerides, diglycerides, and monoglycerides, still contained in beef tallow oil, into methyl esters [27]. The K2O/ACT catalyst assists the transesterification process, which produces K2O compounds that function as the catalyst's active site.

The formation of the active side of the heterogeneous base catalyst (KOH) causes a reaction with methanol in the transesterification process to produce methoxide ions, which have strong nucleophile properties. According to research by Umam (2018) [28], methoxide ion is a strong base with high catalytic properties in transesterification reactions. Therefore, active methoxide ions can attack the carbonyl groups on triglycerides, forming intermediates. These intermediates then undergo rearrangement and produce diglycerides. The following process is similar to the triglyceride reaction. Similarly, figure 2 explains the mechanism of the transesterification reaction.

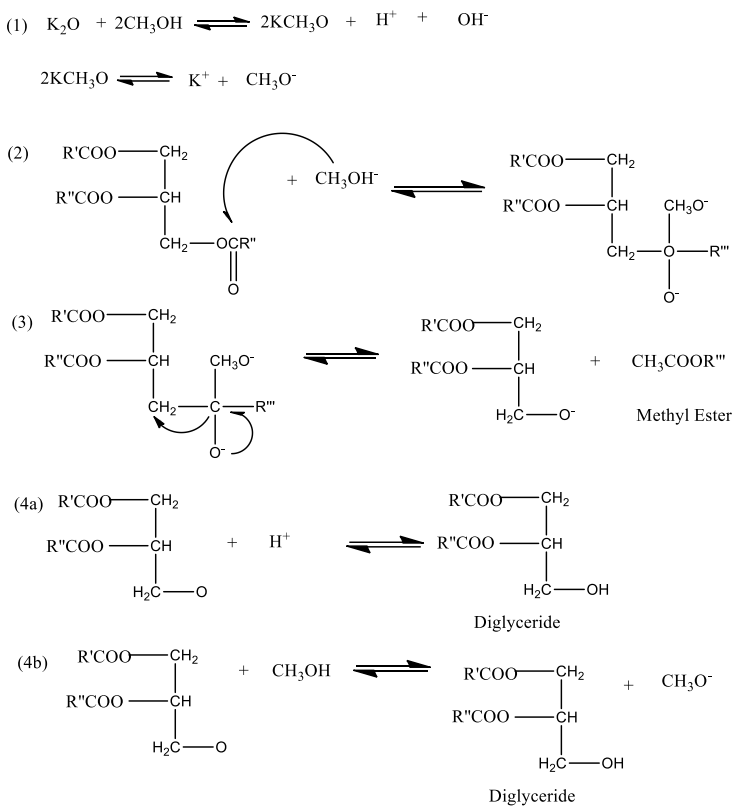

Figure 2. Transesterification reaction mechanism

After the transesterification process, three layers are obtained: catalyst, methyl ester, and glycerol. The method of separating biodiesel and catalyst by filtering. Then, the resulting filtrate is put into a vial and waited until two layers form. The top layer is biodiesel, and the bottom layer is glycerol. The formation of these two layers is due to the difference in density of biodiesel and glycerol. Then, the resulting biodiesel is heated at 105 ℃ to evaporate the water and remaining methanol. Then, the resulting biodiesel is weighed to calculate the resulting yield before being analyzed by GC-MS, as in Table 2.

Table 2. Comparison of Percent Biodiesel Yield

Comparison of Catalyst Weight (gr)	Yield (%)	FAME GC-MS (% Area)
ACT (5,6)	55.05	98.84
K_2O/ACT (0,169: 5,6)	61.27	98.40

Based on Table 2, increasing the percentage of catalyst can increase the yield in a chemical reaction. This is caused by several factors, including adding a catalyst, which can speed up the response by reducing the activation energy so that the reaction process runs more efficiently and produces more products. Apart from that, adding a catalyst can also influence the conversion of reactants into products, ultimately increasing the yield.

Next, the FAME content and composition in biodiesel products were characterized using Gas Chromatography Mass Spectrometry (GC-MS). The results of the GC-MS spectrum of biodiesel products are presented in Figure 3. Meanwhile, the identification of components and composition of biodiesel products derived from the GC-MS spectrum are listed in Table 3.

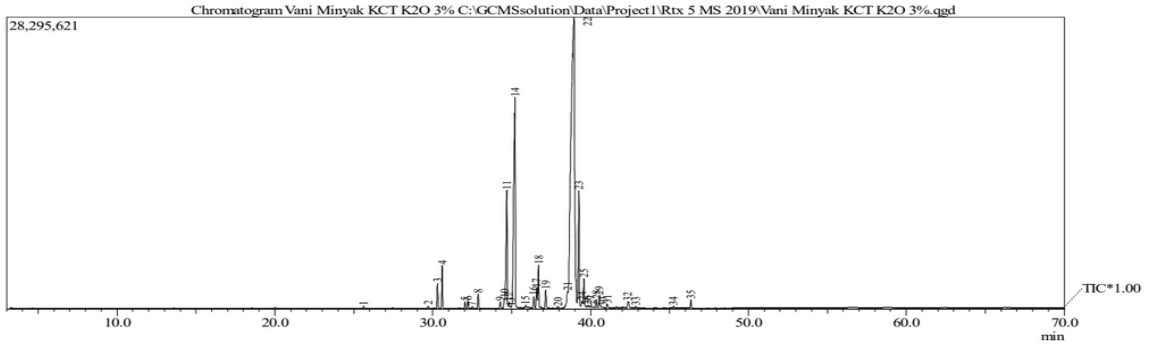

Figure 3. GC-MS chromatogram of biodiesel product

Table 3. Identification and composition of the biodiesel product using GC-MS

Methyl ester compounds identified	CaO	K_2O/ACT
Methyl oleate	52.93	55.69
Methyl palmitate	27.69	28.39
Methyl stearate	9.3	7.95
Methyl linoleate	1.91	1.78
Methyl myristate	2.18	0
Methyl nonadecylic	0.3	0
Methyl pentadesilat	0.75	1.2
Methyl arakidat	0.36	0.4
Methyl lignoceric	1.02	0
Methyl isoleate	1.74	1.9
Methyl paulinat	0.66	0.7
Methyl laurat	0	0.09
Methyl pentakosanoat	0	0.06
Methyl behenate	0	0.24
Total % area FAME	98.84	98.4

The three highest methyl ester compounds found were methyl oleate, palmitate, and stearate. This is by research conducted by Prastyo, Ibrahim, and Solikha [29], which states that biodiesel's highest methyl ester content is methyl oleate, methyl palmitate, and methyl stearate [29]. The reason methyl oleate appears first compared to the saturated fatty acid methyl palmitate is the length of the carbon chain, where saturated fatty acids with shorter carbon chain lengths, such as methyl oleate, may be easier to arrange in triglycerides. Apart from that, a third methyl stearate appears because the molecular weight of methyl stearate is greater than that of other saturated fatty acids. This causes methyl stearate to have a longer retention time so that the methyl stearate peak appears last in the gas chromatography analysis.

Conclusion

Making Biodiesel using K_2O/ACT catalyst impregnation successfully obtained K_2O compounds from XRD analysis with an intensity of 33.9821° and BET analysis with a surface area of 10.487 m^2/g. Results of K_2O/ACT catalyst activity in the transesterification reaction of beef fat into biodiesel with the largest methyl ester content, namely 98.40%

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