Preparation Of KF-Modified Kaolinite As Green And Reusable Catalyst For Microwave Assisted Biodiesel Conversion

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Abstract. Preparation of KF-modified kaolinite catalyst for microwave-assisted biodiesel conversion has been investigated. Kaolinite modification was conducted by solid-solid reaction between naturally occurring kaolinite mineral and KF salt followed by heating at 200°C for 2h. Prepared catalyst was characterized by using XRD, BET surface area analyzer, and SEM-EDX analysis and for catalytic activity tests, biodiesel conversion of jatropha oil was simulated. The comparison between microwave utilization and conventional method of biodiesel conversion were studied, moreover study on the catalyst reusability was performed. The results show that prepared catalyst gives the better physicochemical character of kaolinite as heterogeneous catalysts application as shown by the higher conversion and also reusability. Furthermore, the use of microwave irradiation exhibits the more time effectiveness. In general, the greener biodiesel conversion using presented methods is promising technique to be developed.

1. Introduction

Indonesia has huge world’s natural resources particularly plants and minerals. In another side, fuel is a natural resource that could not be renewed, and one day it might be limited sources. Therefore the peoples try to initiate and develop alternative fuels. One of the alternative fuels is biomass based such as biodiesel. Biodiesel can be used as an alternative fuel diesel engines, and that is environmental friendly[1]. Biodiesel is produced from vegetable oils or animal fats over catalytic reaction. Vegetable oil is a raw material potential as a source of biodiesel because of its presence can be renewed. Vegetable oils used for biodiesel production including corn oil, cashew oil, coconut oil, sunflower oil, olive oil, soybean oil and castor oil have been reported[2]. The reaction requires a catalyst to accelerate the reaction for increasing the rate. The Homogenous catalyst of NaOH is usually applied, and it leads problems related to non-regenerable and consumable properties. Such condition affects to in sustainable process refer to green chemistry principles this research offers an environmentally friendly catalyst, i.e., heterogeneous catalyst[1–9]. Due to the very big potency of natural mineral in Indonesia, utilization of natural kaolinite as raw material for heterogeneous catalysts is an interesting
topic. Refer to basic mechanism of biodiesel conversion and reaction a base catalyst plays an important role in the mechanism[6]. Some improvements have been attempted for increasing the effectiveness of the solid catalyst in such biodiesel conversion, and an effort can be applied the modification with a salt consisting very basic anion[10]. Such modifications of solid basic catalysts were reported by previous papers. The addition and composite formation of a solid catalyst with potassium salt of KF, K₂CO₃ and KOH were attempted by the main mechanism of the improvement of solid basicity for increasing activity of the catalysis[11–14].

In this study, the modification of kaolinite with KF has been applied. Calcium Flouride (KF) was hypothesized to increase the basicity as well as biodiesel conversion rate. Another scheme for the benign environmental process the reaction will be accelerated over microwave assisted reaction. Some reports investigated the feasibility of microwave irradiation procedure in some organic conversion including biodiesel, and it gives some advantageous refer to time-effective and energy efficiency[15,16]. By a combination of the potency of kaolinite modification and the use of microwave irradiation, this study is aimed to evaluate the effect kaolinite modification onto physic-chemical character especially catalytic activity in biodiesel conversion over microwave utilization[1,4,17].

2. Materials and Method

2.1. Materials
Materials used in this research are castor oil supplied from National Company in Indonesia, natural kaolinite from Sukabumi West Java, KF, methanol, citric acid, NaOH were purchased from Merck, Germany.

2.2. Methods
KF/Kaolinite(KF/KAO) was prepared by grinding method. KF and kaolinite powder were mixed and grinded for 20 minutes, before heating at 200 °C for 2 hours.

Prepared and raw material were characterized by XRD, Gas Sorption Analyzer, Scanning Electron Microscope – Energy Dispersive x-Ray (SEM-EDX). XRD X6000 Shimadzu was utilized for XRD measurement with Ni-filtered Cu-Kα radiation. For surface profile measurement, NOVA 1200e instrument was employed by using N₂ gas adsorption at the temperature of 77K, while for SEM-EDX a JEOL instrument was utilized. Surface basicity of the materials was determined by using back-titration method. The tested material was mixed with excess citric acid solution under stirring for a night. The unreacted citric acid was determined by titration using NaOH solution as a standard. The basicity was calculated from the sorbed citric acid per mass of the material (meq/g).

For catalytic activity test, 20 ml of castor oil was mixed with 60 ml of methanol, and 2 grams of catalyst (KAO and KF/KAO). Two variations of reaction system were applied: (1) microwave(MW) irradiation system (reactor set up is presented in Figure 1) for 30 minutes, (2) conventional method by refluxing the mixture for 2 hours. Results of the reactions were separated in separating funnel and the biodiesel fraction was analyzed by using GC-MS instrument. The calorific value of products was analyzed using Bomb-Calorimeter method.
3. Results And Discussion

3.1. Catalyst Preparation and Characterization

XRD analysis was used to identify and characterize the crystallinity of material. The XRD results can be displayed on the diffractogram in Figure 2.

![Figure 2. XRD pattern of KF/KAO and KAO](image)

Figure 1. Microwave Reactor

Figure 2. XRD pattern of KF/KAO and KAO
From the XRD pattern, it is showed that there some peaks in stare of kaolinite reflection at (002). Some impurities were detected i.e monmorilonite (MMT) and quartz (Q). It is because the materials used as raw material is natural kaolinite. From the comparison of both reflection it is concluded that there is no significant change of the reflection after the modification[8].

In order to evaluate the change of surface profile after KF modification, gas sorption analysis of the material was conducted by analyzing N\textsubscript{2} adsorption-desorption. The profile is depicted in Figure 3 and calculated parameters is listed in Table 1.

Isotherm graph in Figure 3 confirm that adsorption isotherm obey type III [9]. It theoretically describes that the BET adsorption of gas molecules on the surface of solids will absorb in physisorption. In the adsorption process, nitrogen gas forms the multilayer region of molecules adsorption on the kaolinite surface and the monolayer region will be used to determine the specific surface area and pore size distribution that exist on the catalyst. The graph shows that KF/KAO gives higher volume of adsorption in all pressure region compared to KAO. From the pattern, specific surface area, pore volume and pore radius were calculated and the data are presented in Table 1. Both the curves and calculated data suggest that the modification of KF into the surface of KAO open the silica alumina surface. In addition the surface basicity of the materials which is the important parameter for trans esterification reaction also indicates the formation of basic interaction of attached F from KF to the surface as KF/KAO exhibits the higher value.
Data in Table 1 shows that after KF modification the surface area and pore volume were increased. The surface area is an important parameter which is referred to the texture of the surface design from heterogeneous catalysts. Related to the pore structure of the particles, pore shape and pore size distribution. The total surface area will be an important criterion to demonstrate the solid catalyst active sites that are directly related to the activity of the catalyst. Then the properties of the pore can control the movement of molecules related to selectivity. High selectivity becomes an important factor in biodiesel conversion.

Surface profile of KAO and KF/KAO was exhibited by SEM-EDX (Figure 4).
3.2. Catalytic Activity Test

For catalytic activity testing, biodiesel conversion offers prepared materials was conducted. To evaluate the effect of conversion method (Conventional and MW) and catalysts condition (fresh and reuse), the volume and methyl esters percentage are reported (Table 2).

The mechanism of transesterification in the biodiesel conversion over heterogeneous catalyst can be schematically represented by the following reaction:
The yield (%) of biodiesel was calculated from GCMS data by identifying the percentage of methyl ester formed (5). The test is also conducted for reused catalyst. After was separated from the reaction mixture, used catalyst was washed with methanol followed by drying. Regenerated catalyst was further reused for the same reaction.

Table 2. Catalytic Activity Data of Materials by Variation Methods and Catalysts Condition

| Catalyst       | Reflux | MW     |       |       |       |       |       |       |
|----------------|--------|--------|-------|-------|-------|-------|-------|-------|
|                | Volume (mL) | Yield (%) | Calorific value (Kcal) | Volume (mL) | Yield (% Ester) |       |       |       |
|----------------|-----------|-----------|------------------------|-------------|------------------|-------|-------|-------|
| KAO            | 16.4      | 45.67     | 3883.61                | 13.5        | 58.90            | 10922.90 |       |       |
| KF/KAO         | 15.60     | 61.92     | 3391.49                | 13.20       | 72.15            | 8029.04 |       |       |
| KAO-reuse      | 11.7      | n.d*      | 4315.80                | 10.4        | n.d              | nd     |       |       |
| KF/KAO-reuse   | 10.0      | n.d       | 8552.95                | 9.8         | 15.10            | 3579.58 |       |       |

n.d= non detected

Table 2 shows that in general MW method gives higher yield compared to the conventional one. It is also confirmed that reusability of KF/KAO better than KAO as well as the utilization of MW gives better reusability from the produced methyl ester. The objective of sustainability in the proposed method is gained since the catalyst can be reused for further process.

4. Conclusions
Based on the results KF/KAO was successfully prepared with increasing parameters. The modification on KAO expressed the increasing activity in biodiesel conversion over microwave irradiation method. Compared with the conventional method, MW method gives the advantageous related to energy an efficient, time value of 12 hours which requires a very long time reaction is on a large scale. Production of biodiesel by microwave is effective and need to be developed so it can be a solution to the energy crisis currently.

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