CATALYTIC ACTIVITY OF PRECIPITATED CALCIUM CARBONATE FOR BIODIESEL PRODUCTION

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ABSTRACT

Transesterification of used cooking oil (UCO) with methanol using calcium carbonate precipitate (PCC) as a heterogeneous catalyst was carried out under reflux with constant stirring to obtain biodiesel. Before the catalyst test, PCC was first thermally activated at 900 °C for 5 hours to obtain CaO. and then characterized by X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF) and Scanning Electron Microscopy (SEM). The effects of temperature, reaction time, methanol/oil molar ratio and amount of catalyst were investigated. The highest yield of biodiesel produced was 93% after 4 hours reaction time using 5%wt catalyst and methanol to oil ratio 6:1. In addition, the catalyst has good reuse potential for the synthesis of biodiesel.

Keywords: Biodiesel, Heterogeneous Base Catalysts, Used Cooking Oil, Transesterification, PCC.

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INTRODUCTION

One present technological challenge is finding ways to reduce fossil fuel use while increasing energy requirements. Therefore, to replace petroleum-based fuels, clean and renewable energy needs to be developed.¹ One such well-researched renewable and environmentally friendly substitute for fossil fuel is biodiesel.² which has economic, technical, and environmental advantages.³ Previous research has shown that vegetable oil can be utilized as engine fuel if diluted, used in a microemulsion, or processed using thermal cracking (pyrolysis), or transesterification.⁴ Of these transesterification is most popular because of its low cost, transesterification to obtain biodiesel usually consists of a reaction between triglycerides and alcohol in the presence of a catalyst.⁵ The moisture content of oil or fat, free fatty acids, the molar ratio of alcohol: oil, type of catalyst, amount of catalyst, reaction temperature, and reaction time affect the transesterification reaction.⁴ Triglycerides from vegetable oils and short-chain alcohols are the raw material for biodiesel production. The use of virgin vegetable oil directly raises problems related to food competition.⁶ However, waste cooking oil can be used as an alternative.

The catalyst plays an important role in the transesterification reaction.⁷ A biodiesel synthesis catalyst can be homogeneous or heterogeneous.⁸ High biodiesel yields are obtained by using a homogeneous catalyst but the process can be expensive due to saponification, excessive use of chemicals, and additional costs for separation.⁹ Heterogeneous catalysts, on the other hand, have been developed that are also efficient, prevent saponification, and can be separated and reused easily.¹⁰ CaO is one such catalyst. CaO can be obtained easily from limestone derivatives, waste eggshell, oyster and other sea shells.¹¹ CaO has high alkalinity, low solubility in methanol, and high catalytic activity.¹²

This research explores the use of precipitated calcium carbonate (PCC) as a heterogeneous base catalyst for biodiesel production. The precipitated calcium carbonate is sourced from limestone, which is rich in calcium carbonate (CaCO₃). A simple calcination process at high temperatures converts it into calcium oxide (CaO), which is cost-effective and environmentally friendly. The use of precipitated calcium carbonate for the preparation of CaO catalysts comes from limestone obtained from the Lintau Buo area, West Sumatra. The effects of catalytic activity were investigated in the transesterification reaction of Edible Oil Waste for biodiesel production.

EXPERIMENTAL

Material

Limestone was collected from Lintau Buo, West Sumatra. Used cooking oil (already used for frying three times) collected from sellers of fried food in Jati Padang, West Sumatra and its chemical composition was analyzed by GCMS. The methanol, ethanol, n-hexane used were purchased from Merck Limited, Padang, Indonesia.

Catalyst Preparation

The collected limestone was washed thoroughly to remove surface dirt using distilled water and dried at 105 °C. Then limestone was mashed and calcined in a 900 °C furnace for 5 hours. 20 g of the CaO obtained was dissolved in 300 ml of 2 M HNO₃, stirred for 30 minutes, then filtered. NH₄OH was added to the filtrate at 60 °C until it reached pH 12. The solution was filtered and CO₂ gas was passed through it at pH 8. The precipitate formed was filtered and washed with distilled water then dried at 100-115 °C for 2 hours¹³. Precipitated calcium carbonate was calcined in a 900 °C furnace for 5 hours.

Catalyst Characterization

The crystal structure of the catalyst was determined using powder X-ray diffraction (XRD) using a Pan Analytical Expert Pro X-ray diffractometer equipped with Cu K α radiation. Elemental analysis was carried out using X-ray fluorescence (XRF) using an Epsilon PANalytical Model 3. Morphological analysis of the catalyst was analyzed using Scanning electron microscopy (SEM) supplemented with X-ray spectroscopy (EDX) JEOL energy scattering, JSM-6290LV.

Transesterification

Used cooking oil was initially filtered with Whatman filter paper no. 42 to remove frying debris and heated until constant weight. The transesterification reaction was carried out in a 500 ml triple-necked flask with a reflux condenser and a magnetic stirrer. First, the catalyst was activated with the addition of methanol and stirring. A measured amount of 100 °C used cooking oil added and the reaction carried out under the selected conditions. After the reaction was complete, the solid catalyst was filtered using a funnel with filter paper. The filtrate was transferred to a separating funnel and left to stand overnight. The lower layers were discarded, and the upper layers were collected. The resulting biodiesel was rinsed with hot distilled water until the washing water looked clear then dried at 110 °C to remove the washing water. After that biodiesel was analyzed by gas chromatography and the yield calculated using the following formula:

$$\text{Yield of Biodiesel (\%)} = \frac{\% \text{Area Gc Biodiesel} \times \text{Weight of product}}{\text{weight of Used Cooking Oil}} \times 100\%$$

RESULTS AND DISCUSSION

Catalyst Characterization

X-Ray Diffraction Analysis (XRD)

The XRD pattern obtained from the raw and calcined PCC is presented in Fig.-1. The main characteristic peaks at $2\theta = 22.99^\circ, 29.34^\circ, 35.93^\circ, 39.37^\circ, 43.12^\circ, 47.46^\circ$ and 48.47° , corresponding to the calcium carbonate (CaCO₃) phase, are found in the crude PCC XRD pattern indicating the presence of CaCO₃ in PCC. These results are also consistent with the XRF analysis presented in Table-1, showing that calcium is the main element in the PCC sample. The calcined PCC sample showed peaks corresponding to the CaO (ICDD 01-077-2376) phase ($2\theta = 32.19^\circ, 37.35^\circ, 53.84^\circ, 64.13^\circ, 67.36^\circ, 79.63^\circ, 88.49^\circ$ and 91.43°) and to Ca (OH)₂ (ICDD 00-044-1481) ($2\theta = 18.06^\circ, 28.67^\circ, 34.10^\circ, 47.14^\circ, 50.79^\circ, 54.35^\circ, 62.60^\circ$ and 64.29°), which indicates that CaCO₃ changes to CaO after calcination.¹⁴

The XRD results from the recycled catalyst (Fig.-1) shows a peak at ($2\theta = 13.64^\circ, 15.25^\circ, 20.21^\circ, 21.43^\circ$) indicating that some CaO is changed to calcium glyceroxide, Ca (C₃H₇O₃)₂ (ICDD 00-021-1544). This new phase is formed by a reaction between CaO with the glycerol resulting in the transesterification reaction.¹¹

Fig.-1: X-ray Diffraction Analysis (A) PCC (B) PCC Calcined 900°C (C) after one cycle of use

X-ray Fluorescence Analysis (XRF)

Pre and post 900 °C calcination PCC composition was analyzed by XRF (Table-1). The pre calcination PCC sample was found to be 97% Ca which increased to 98% after calcination. After being used for the first transesterification process, Ca content decreased to 91% due to the reaction of CaO with glycerol forming calcium glyceroxide as previously reported.¹¹

Table -1: X-ray Fluorescence Analysis (A) PCC (B) PCC Calcination at 900°C (C) after one cycle of use

Compound	A	B	C
	Conc	Conc	Conc
CaO	97.2	98	91.4
SiO ₂	0.2	0.6	2.3
Al ₂ O ₃	0.6	0.5	1.4
MgO	0.1	0.0	0.0
Fe ₂ O ₃	0.1	0.0	0.6
Ag ₂ O	0.8	0.7	0.5

SEM Analysis

The morphology of PCC that had been calcined and after the first transesterification process can be compared in Fig.-2) at the same magnification. Morphological changes on the surface of the catalyst are evident. Initially, PCC had a uniform and regular distribution of particles but after being used as a catalyst in the transesterification process larger particles are evident. This happens because intermediate products such as diglycerides, monoglycerides, glycerol or biodiesel clogged the catalyst pores causing the loss of active sites and reducing subsequent catalytic activity.¹⁵

Fig.-2: SEM of PCC (A) Before use as a Transesterification Catalyst (B) After one cycle of use

Catalytic Activity in Transesterification

The catalytic activity of calcined PCC was evaluated for the following reaction parameters: the amount of catalyst, the molar ratio of methanol to oil, reaction time and temperature.

Amount of Catalyst

The effect of the amount of catalyst (1,3,5 or 7 wt%) was investigated on reactions at 65 °C for 4h using a 6: 1 methanol: oil ratio. Results are shown in (Fig.-3). Calcium oxide plays an important role in making methanol a more reactive nucleophile (anion methoxide) species that will attack the carbonyl groups in triglycerides.¹⁶ It was found that up to 5wt% the more CaO catalyst added the higher the yield of biodiesel. Increasing CaO after this optimum value had been reached resulted in reduced yields due to secondary reactions of the catalyst with reactants.¹⁷

Fig.-3:Effect of Catalyst Amount on Yield

Ratio of Methanol to Oil

The ratio of methanol to oil significantly affected the yield. Experiments to test the ratios 3: 1, 6: 1, 9: 1 and 12: 1 of methanol to oil were carried out at 65 °C for 4h using 5wt% catalyst. Figure-4 shows that the yield of biodiesel increases with increasing ratio of methanol to oil up until an optimal value at 6: 1. Higher concentrations of methanol accelerate the formation of methoxide species on the catalyst surface so shifting the equilibrium towards the formation of methyl esters.¹⁸ However, biodiesel yields begin to decrease when the ratio of methanol to oil exceeds 6:1. Transesterification is a reversible reaction and the solubility of the by-product glycerol increases with excess methanol.¹⁹

Fig.-4:Effect of Methanol Oil Molar Ratio on yield

Reaction Time

The effect of 2, 4, 6 and 8 h reaction times on the yield of biodiesel production is shown in (Fig.-5). These reactions were at 65 °C and used 5wt% of catalyst and a methanol: oil ratio 6: 1. The optimal reaction time was found to be about 4 hours. The yield of biodiesel was low for short reaction times because the use of heterogeneous catalysts does not result in a fast reaction.²⁰ Yield increased up to a reaction time of 4 hours. After that, a white gel began to form due to saponification which affected the purification process and increased the viscosity of the product.²¹

Fig.-5:Effect of Reaction Time on yield

Effect of Temperature

The effect of 55,60,65 and 70°C reaction temperatures on yield was investigated using reaction 5wt% catalyst, methanol: oil ratio 6: 1 and 4h reaction durations as shown in (Fig.-6). It was observed that temperature had a positive effect on methanolysis from used cooking oil. The yield of biodiesel increased significantly as the reaction temperature increased up to 65 °C. However, a reaction temperature exceeding this optimal value reduced biodiesel yield. In general, an increase in temperature increases kinetic energy which results in more and harder collisions between reactant molecules.²² This can increase miscibility and mass transfer between reactants. However, exceeding the optimum conditions causes methanol to evaporate and reduces its concentration.²³

Fig.-6:Effect of Reaction Temperature on Yield

Reusability

Heterogeneous catalysts can be recovered and reused to reduce production costs.²⁴ To test reusability reactions were conducted under optimal reaction conditions. Fresh reactants were used then, after the reaction, collected using filter paper and washed using n-hexane and methanol to remove impurities.²¹ It can be seen from (Fig.-7) that the biodiesel yield decreased from 92.7% to 59.1% when the same catalyst was reused over four reaction cycles.

Fig.-7:Reusability Test results

This reduced biodiesel yield is due to reduced catalytic activity as some of the calcium oxides are lost in the washing of active species.¹⁰ Also, some catalyst deactivation occurs as catalyst pores are blocked by intermediate products including diglycerides, monoglycerides, glycerol and biodiesel reducing contact between the catalyst and the reactant mixture.¹⁷

CONCLUSION

PCC from limestone is the source of an effective CaO heterogeneous catalyst for the transesterification of waste cooking oil after 900 °C calcination for 5 hours. The reaction time, reaction temperature, and ratio of methanol to oil are the parameters investigated. The maximum yield (92.7%) of biodiesel was obtained at 65°C using 5% by weight catalyst, methanol to oil ratio of 6: 1 and reaction time of 4 hours. Viable amounts of catalyst remained for three cycles of reaction.

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