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Application of Response Surface Methodology for Biodiesel Synthesis Optimization Through Transesterification Reaction using h-zeolite/ki Heterogeneous Catalyst

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Abstract. Biodiesel production based on crude palm oil (CPO) using heterogeneous catalysts is a new hope for solving the energy crisis. One type of heterogeneous catalyst is H-Zeolite/KI synthesized from natural zeolite impregnated with 0.05% (w/v) KI compound for 2 hours. The research focuses on determining the optimum operating conditions for biodiesel production using H-zeolite/KI catalysts. As raw material used CPO which has pre-treatment through an esterification reaction using 15% H_2SO_4 (w/v) as catalyst, temperature 65°C, stirrer speed of 400 rpm for 2 hours to reduce the free fatty acid content of raw materials up to 40%. Optimization of biodiesel production is carried out at the transesterification reaction. The research data was designed following the Response Surface Methodology (RSM) method using 3 independent variables and 5 levels, namely the ratio of H-zeolite/KI catalyst, transesterification temperature and mole methanol: CPO ratio with coded level (-1.682), (-1), (0), (+1), (+1.682). The research results show that the optimum operating conditions of biodiesel production were at the ratio of H-zeolite/KI catalyst at 2% - 2.5% (w/w), temperature at 45°C-50°C and mole ratio of methanol: CPO at (1:6). The biodiesel product was confirmed using gas chromatography and showed ester content of 88.02%. Characteristics of biodiesel products showed flash point 130C, acid number 0.4%, glycerol free 0%, viscosity 3.6 cP, density0.879 gr/cm^3.

1. Introduction

The depletion of fossil resources causes the use of renewable resources to be an option. The mass utilization of biofuels from vegetable oil in internal combustion engines dates back to the early 20th century (1920-1930) in particular during war world II, with reported use from around the globe including Germany, Argentina, Japan, Belgium, Italy, France, the United Kingdom, Portugal, and China whom all tested and used various types of biofuels [1]. However, the emergence of low cost petroleum fuel production caused a decline in biofuel research and made investigation into the biofuel production infrastructures redundant. In recent times concern over the depletion of the finite fossil fuel

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reserves and with the transport sector now accounting for approximately 25% of the overall energy consumption and CO_2 equivalent emissions produced globally a resurgence is being witnessed in biofuel research and utilisation [2].

The development of the biofuel industry especially biodiesel is very promising because of the availability of raw material sources. Catalysts for transesterification could be either homogenous or

heterogeneous one. A main drawback of the homogeneous catalyst is that a large amount of washing water is required. On the other hand, an advantage of the heterogeneous catalyst is an ease of catalyst separation and reusability [3,4].

One type of heterogeneous catalyst is zeolite. Zeolite are high surface area materials that have been widely used in areas such as water treatment and purification, humidity control, and heterogeneous catalysis [2]. To date, the majority of established synthesis have used artificial reagents by heating a solution of some form of silica, alumina and alkylammounium salts in water, which over time forms a solid precipitated aluminosilicate zeolite [3]. Zeolitemay also be prepared from naturally occurring reagents. Clays, rocks and ash residues from combustion of solid fuels contain large amounts of oxygen, silicon and aluminum that have similar chemical compositions to those of some aluminum silicate zeolites.

In this research zeolite catalysts were synthesized from natural zeolite from Ujung Pancu, Aceh Besar and prepared with KI compounds to activate the nucleus of zeolite. After that, calcination is done to form a strong bond between the KI core and zeolite pore.

2. Raw Material

The raw materials used are crude palm oil (CPO) as the triglyceride source, Methanol (p.a), zeolite/KI as the heterogeneous catalyst, H_2SO_4 98%, NaOH (p.a), hexane, ethanol. CPO as the main ingredient analysed free fatty acid to know the initial free fatty acid content.

3. Methods

CPO is reacted with methanol using H_2SO_4 catalyst to form crude ester. The ester content in the crude ester obtained will be optimized through the transesterification reaction using H^+ zeolite catalyst. Optimization is done using the Response Surface Methodology method using 3 variables and 5 levels.

In this study, a two-stage reaction was carried out to convert crude palm oil into esters (biodiesel). The first stage is esterification and the second stage is transesterification. Esterification was carried out by reacted CPO and methanol with H_2SO_4 as catalyst. After two hours, CPO has been converted to crude ester at least 40%-50%, but it is not meet a standard to be used as biofuel. So, to increase the ester content, the crude ester has to be reacted by transesterification using H-zeolite/KI.

3.1. Transesterification

The transesterification reaction is also called alcohollization, is the conversion stage of triglyceride (vegetable oil) to alkyl ester, reacted with the alcohol to produce a by-product of glycerol. The CPO from esterification reaction is referred to crude ester. It is used as a feedstock in the transesterification reaction. Crude ester is reacted with methanol with the addition of zeolite/KIas heterogeneous catalyst. Optimization of production will be carried out at the transesterification stage using 3 variables and 5 levels i.e. zeolite ratio, temperature, and ratio mole of CPO: methanol.

3.2. Experimental Design

Optimization aims to determine the optimum operating conditions in CPO-based biodiesel production using heterogeneous H-zeolite catalyst. The optimum condition of the research was known based on the interaction between the three independent variables, namely the interaction between the zeolite ratio, the CPO: methanol mole ratio and the reaction temperature.

Optimization research was designed using the central composite design (CCD) method and analyzed using response surface. In the CCD design, the center point is needed for each independent variable that is used as an influence in the study. The center point value is obtained through preliminary research that has been done previously. Center point values are arranged as follows. The Central Composite Design (CCD) design for 3 process variables with initial response is ester content.

Table 1. Central Composite Design (CCD)

Variables	Coded Treatment				
	-1.682	-1	0	1	1.682
Ratio of Zeolite	1.659	2	2.5	3	3.341
Temperature of Transesterification	37	40	45	50	54
Ratio mole CH_3OH: CPO	0.954	3	6	9	11.045

Table 2. *Central Composite Design* (CCD) For 3 Variables

No	Ratio of Zeolite/KI (% w/w)		Temperature of Transesterification (°C)		Ratio CPO: Methanol (Mole)		Ester Content (%)
	Actual	Code	Actual	Code	Actual	Code	
1	2	-1	40	1	3	-1	
2	3	1	40	1	3	-1	
3	2	-1	40	-1	3	-1	
4	3	1	40	-1	3	-1	
5	2	-1	50	1	9	1	
6	3	1	50	1	9	1	
7	2	-1	50	-1	9	1	
8	3	1	50	-1	9	1	
9	1,682	-1,682	45	0	6	0	
10	3,341	1,682	45	0	6	0	
11	2,5	0	45	0	6	0	
12	2,5	0	45	0	6	0	
13	2,5	0	37	-1,682	0,954	-1,682	
14	2,5	0	50	1,682	11,045	1,682	
15	2,5	0	45	0	6	0	
16	2,5	0	45	0	6	0	
17	2,5	0	45	0	6	0	
18	2,5	0	45	0	6	0	
19	2,5	0	45	0	6	0	
20	2,5	0	45	0	6	0	

4. Results and Discussion

4.1. Effect of Ratio of H-Zeolite Catalyst and Ratio of Mol CPO: Methanol to the Acquisition of Ester Content

The interaction of the three research variables, namely the ratio of catalyst and the mole ratio of CPO: methanol to the acquisition of ester content can be analyzed using a surface response which will show the level of interaction between variables giving optimum response. From the surface response and contour graphs, it shows that the increase in the ratio of zeolite catalysts and the mole ratio between CPO: Methanol does not have a significant effect on ester content acquisition. When the reaction temperature is at the center point, content ester acquisition is predicted to increase when the ratio of the catalyst is in code (-1) or (<-1) and the mole ratio of CPO: methanol is in code (1) or (>1). Actually, zeolite catalysts can be used in the range of 1.659% to 2% (w/w), and the mole ratio of CPO: methanol ranges (1:9) to (1: 11.045) or is increased to obtain optimal ester content.

From the surface response and contour graphs, it shows that the increase in the ratio of zeolite catalysts and the CPO mole ratio: Methanol does not have a significant effect on ester content acquisition. When the reaction temperature is at the center point, content ester acquisition is predicted to increase when the ratio of the catalyst is in code (-1) or (<-1) and the mole ratio of CPO: methanol is in code (1) or (> 1). Actually, zeolite catalysts can be used in the range of 1.659% to 2% (w/w), and the mole ratio of CPO: methanol ranges from (1: 9) to (1: 11.045) or is increased to obtain optimal ester content acquisition.

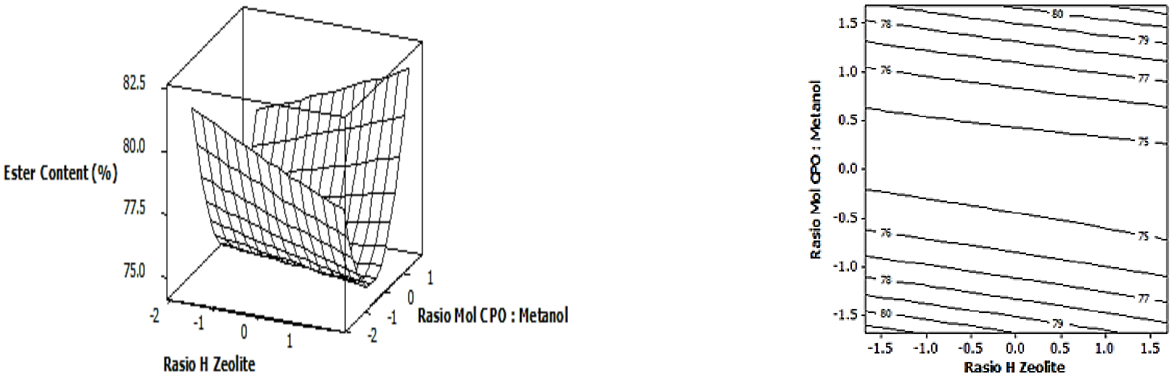

Figure 1. Graph Effect of Ratio of H-Zeolite Catalyst and Ratio of Mol CPO: Methanol to Acquisition of Ester Content

4.2. *Effect of Ratio of H-Zeolite Catalyst and Temperature on Acquisition of Ester Content*

Based on the surface response and contour graphs, it is shown that the increase in zeolite ratio from encoded level (0) to encoded level (1) has an effect on ester content acquisition with temperature interaction at the coded level (1). Actually, the zeolite ratio is in the range of 2.5% to 1% (w/w) with a temperature interaction at 45°C-50°C. The use of zeolite catalyst can reduce the use of high temperatures (65°C). The activity of the zeolite catalyst in the transesterification reaction is quite high as the breaking of the triglyceride chain is faster without requiring high energy without using a high reaction temperature. In the production of biodiesel using NaOH or KOH catalysts, it is carried out at a temperature of 65°C-85°C.Zeolite provides good prospects because it can reduce energy use and production costs.

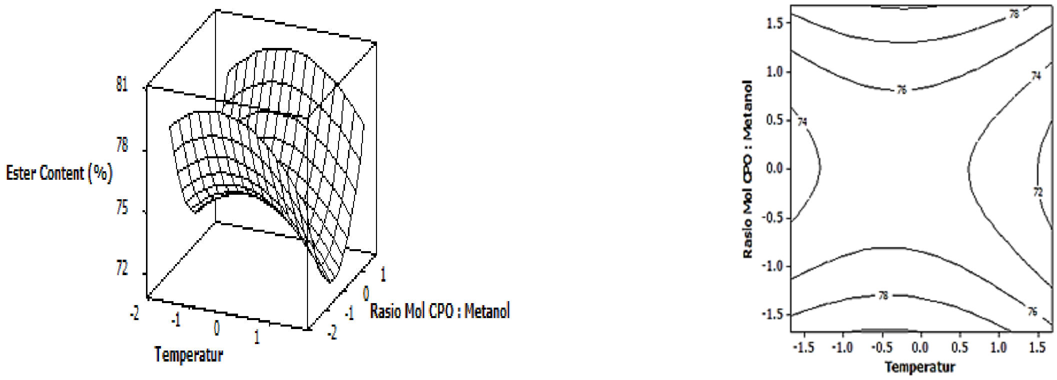

Figure 2. Graph Effect of Mole Ratio of CPO: Methanol and Temperature on Acquisition of Esters Content

In the production of biodiesel, the mole ratio of CPO: methanol plays an important role because the type of alkyl source affects the biodiesel product produced. The interaction between the CPO: methanol and temperature mole ratios in this study can be analyzed through surface response. Based on the results of the analysis, it is known that the encoded level (0) for temperature has a significant effect when interacted with the CPO: methanol mole ratio at the encoded level (0) to (1). In the production of biodiesel with this H-zeolite catalyst, the mole ratio used is very low, which is 1:6 different from the use of a homogeneous catalyst that can reach (1:10) to (1:15). The use of high temperature is also significant, this is due to the good performance of zeolite in the transesterification reaction in breaking the triglyceride chain derived from CPO.

In the consideration of the industrial world, the use of zeolite/KI catalyst in the production of biodiesel is very positive because it can reduce production and energy costs. From the results of the research, it is known that the optimum conditions for biodiesel production are temperatures of 45^{o}C-50^{o}C, mole ratio of CPO: methanol (1:6) and catalyst ratio of 2% to 2.5% (w/w).

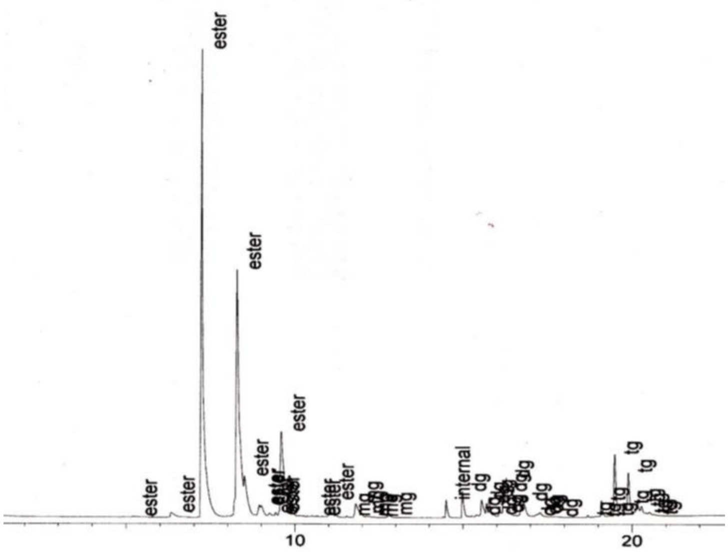

Figure 3. Gas Chromatogram Mass Spectrum

The biodiesel product was confirmed using gas chromatography and showed ester content of 88.02%. Characteristics of biodiesel products showed flash point 130C, acid number 0.4%, glycerol free 0%, viscosity 3.6 cP, density0.879 gr/cm^3.

5. Conclusion

From the results of the study it was found that CPO can be converted into biodiesel using H-zeolite/KI catalyst. The alkyl source used comes from methanol. Zeolite catalysts used as catalysts in the transesterification reaction come from natural rocks containing zeolite. These natural rocks are activated physically and chemically to open zeolite pores and convert zeolite particles into bases and can be used as catalysts in the transesterification reaction. From the results of optimization research, it is known that the optimum conditions for biodiesel production are at a temperature of 45oC-50oC, the mole ratio of CPO: methanol (1:6) and the ratio of zeolite catalyst 2% to 2.5% (w/w). When compared with the use of homogeneous catalysts such as NaOH and KOH, the use of zeolite catalysts is quite effective in terms of energy use and raw materials so as to reduce production costs.

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