

Fluidized Bed Reactor Type: Reactor Design for Biodiesel Production from Soybean Oil Using MgO Catalyst

(Jenis Reaktor Unggun Terfluidakan: Rancangan Reaktor Untuk Produksi Biodiesel dari Minyak Kedelai Menggunakan Katalis MgO)

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Abstract

Biodiesel is one of the solutions to future energy problems. One of the abundant biodiesel raw materials in Indonesia is soybean. This study aims to optimize the yield of biodiesel made from soybean oil by selecting the reactor design. This research method uses literature study and thermodynamic calculations from the transesterification reaction of soybean oil and methanol using a MgO catalyst to determine which type of reactor optimizes biodiesel yield. The type of reactor that can help optimize the yield of MgO biodiesel catalyst is a fluidized bed reactor type with an exothermic reaction and a negative H_f value. There is a higher product concentration than the reaction concentration in the scene because the rate constant is higher than one ($K > 1$), i.e. 1.312. The results of this study are expected to provide information in optimizing the yield of biodiesel from soybean oil.

Keywords: Fluidized Bed Reactor; Biodiesel; MgO Catalyst; Soybean Oil; Transesterification

Sari

Biodiesel merupakan salah satu solusi permasalahan energi di masa depan. Salah satu bahan baku biodiesel yang melimpah di Indonesia adalah kedelai. Penelitian ini bertujuan untuk mengoptimalkan rendemen biodiesel berbahan baku minyak kedelai dengan memilih desain reaktor. Metode penelitian ini menggunakan studi literatur dan perhitungan termodinamika dari reaksi transesterifikasi minyak kedelai dan metanol menggunakan katalis MgO untuk menentukan jenis reaktor yang mengoptimalkan hasil biodiesel. Jenis reaktor yang dapat membantu mengoptimalkan rendemen katalis biodiesel MgO adalah jenis reaktor fluidized bed dengan reaksi eksotermik dan nilai H_f negatif. Konsentrasi produk yang lebih tinggi daripada konsentrasi reaksi karena konstanta laju lebih tinggi dari satu ($K > 1$), yaitu 1,312. Hasil penelitian ini diharapkan dapat memberikan informasi dalam optimasi rendemen biodiesel dari minyak kedelai.

Kata-kata kunci: Reaktor Unggun Terfluidakan, Biodiesel, Katalis MgO, Minyak Kedelai, Transesterifikasi

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I. INTRODUCTION

Indonesia is a major energy consumer in Asian countries, accounting for more than 4% of the energy use area. In 2019, energy consumption growth in Indonesia was 3.96% per year, energy consumption per capita has increased by 24% since 2010, primary energy demand has increased by 4.9% in the last two years, an average of 10 years growing by 2.8 %, energy production grows 3.70% every year [1]. Based on national energy data informs that Indonesia has a lot of energy production, but coal and gas are mostly exported, while for oil products are mostly imported. This is a reality in energy producing countries (11% in Asia) which still depend on fossil fuels due to high energy consumption (4% in Asia) [2].

Biodiesel seems to be a solution to the energy problem faced by reducing the amount of carbon

dioxide released and polluting the atmosphere that contributes to global warming by using fossil fuels. Biodiesel is basically derived from vegetable or animal fats. Biodiesel fuel burns without the emission of large amounts of carbon dioxide and other materials. The transportation and handling of biodiesel is safer than conventional fuels because it has a relatively high flash point and does not produce explosive vapors [3].

One of the abundant biodiesel raw materials in Indonesia is soybean. Soybean has the potential to be used as a source of biodiesel because it contains soybean oil. The advantage of using soybeans as a source of biodiesel is that this plant has been widely grown in Indonesia. Based on this, the availability of soybeans as raw material for biodiesel could be more than jatropha and palm oil [4]. The disadvantage of using soybeans as a source of

biodiesel is that the soybean oil content is only 20%. The percentage of soybean oil content is low compared to other vegetable oil producing plants such as jatropha and palm [5]. One of the efforts to overcome this problem is to design the right reactor and optimize the catalyst for biodiesel production from soybeans.

Fluidized bed reactor (FBR) is a chemical reactor in which particles (catalytic) interact with a gas stream fed from below, so that the mixture (emulsion phase) behaves as a liquid. Reactors of this type are often used in the chemical and process industries, where they have gained popularity due to their excellent heat and mass transfer characteristics. FBR is used for example for gas phase polymerization reactions for producing polyolefins (polyethylene, polypropylene), chemical loop combustion or reforming processes, and gas phase Fischer–Tropsch synthesis. [6]. Parameters such as diffusion or heat transfer are the main design parameters of fluidized bed reactors. Compared with packed bed, fluidized bed has advantages such as better temperature control, no hot spots in the bed, uniform distribution of catalyst, and longer life of the catalyst. The fluidized bed achieves good mixing of the suspended particles and the suspending fluid. In a fluidized bed reactor, the solids or catalytic particles are supported by an upward flow of fluidized fluid. This reactor provides easy loading and unloading of the catalyst. This is advantageous when solid beds need to be changed frequently. High conversion is possible with this type of reactor, the reactor inherently has excellent heat transfer and mixing characteristics. The desirability of using a fluidized bed depends on achieving a good and near perfect mixing of solids and liquid suspensions [7].

The characteristics and properties of the catalyst for biodiesel production are important to determine the reaction rate [8]. Magnesium oxide is used as a heterogeneous base catalyst, as it is a promising catalyst for transesterification [9,10] as well as solids, whose surface structure and reactivity have been extensively studied [11-13]. Heterogeneous catalysts are non-corrosive and result in less consumption of time and chemicals as they can be easily separated from the product due to their high selectivity by filtration and are reusable [14].

Di Serio et al. [15] have conducted research on the use and activity of CHT and MgO base catalysts in biodiesel production, mesoporous catalysts are more active than catalysts containing many micropores for the difficulty of large triglyceride molecules to reach the bottom of the catalytic site in the micropores. This latter finding is relevant from an economic point of view, because to operate imperfectly in a dry reaction environment reduces feedstock pretreatment costs and opens the possibility to use unrefined bio-ethanol. This study aims to design a reactor using a base catalyst that can

be implemented on an industrial scale, the base catalyst used is MgO.

II. METHOD

The use of catalysts has been carried out in small-scale stainless steel reactors. The reaction is carried out by adding reagents (methanol and soybean oil) with the amount considered for each reactor. The transesterification reaction of Soy Bean oil with methanol was carried out in a fluidized bed reactor (FBR) using a MgO catalyst, as shown in Figure 1.

The basic information used in the design of the Fluidized bed reactor for this transesterification reaction is exothermic operating conditions, the reaction takes place at a temperature of 300°C. Solid base catalysts such as ZnO, CuO, zeolite, CaO, SrO, MgO, BaO, basic polymers, and carbonates such as MgCO₃, CaCO₃, BaCO₃, and SrCO₃ have attracted interest as heterogeneous transesterification catalysts. Dossin et al. [16] investigated that MgO has the capability to produce 500 tons of biodiesel in batch reactors through transesterification reaction while maintaining the ambient temperature. Biodiesel manufacturing cost is decreased in batch reactors owing to the application of ambient temperatures. Some researchers have revealed that MgO catalyst can give 91% fatty acid methyl ester (FAME) yield in supercritical condition (300°C) as well as at a high methanol to oil molar ratio (39.6 : 1) [15].

Base catalysts are especially appropriate for good purity oils with low FFA contents because they are more vigorous than acids in transesterification. Continuous flow and a packed bed arrangement are generally employed for synthesizing biodiesel using a solid base catalyst which ultimately facilitates both coproduction of glycerol with good purity and catalyst separation, thus lessening the production cost and promoting the use of the catalyst again [17].

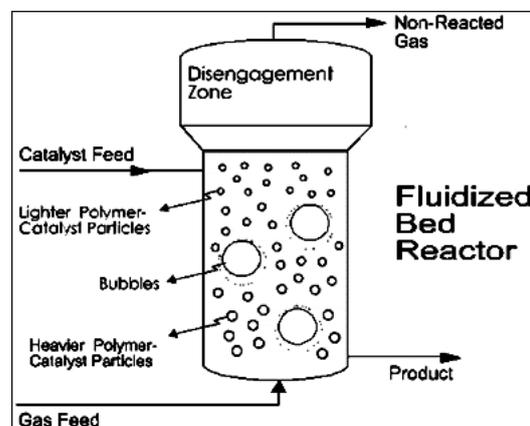


Figure 1. Design fluidized bed reactor. Image adapted from from F. A. Fernandes and L. M. Lona [18].

The model is assumed to have a production

capacity of 80,000 tons per year, 242 tons per day. The ratio of the amount of soybean oil, methanol, and MgO catalyst is 20:8:1, respectively. Table 1 shows some of the properties of the three types of phases involved in the reaction.

Table 1. Properties of reactants, products, and catalysts used in the transesterification reaction

Liquid Phase					
		Amount (ton per cycle)	Density @ 20°C 1 atm	Viscosity @ 25°C	Diameter (mm)
Reactant	Methanol	74	0.791 g/cm ³	0,544 – 0,59 mPa·s	-
	Soybean oil	185	0.91 g/cm ³	0.0386 Pa·s	-
Product	Glycerol	-	1.261 g/cm ³	1.412 mPa·s	-
	Biodiesel	-	7.3 g/cm ³	-	-
	Water	-	0.99823 g/cm ³	0.899 mPa·s	-
Solid Phase					
Catalyst	MgO	9.25	3.58 g/cm ³	-	2x10 ⁻⁵
Gas Phase					
Inert	Nitrogen	-	1,1606 g/ml	1.66 Pa·s	-

III. RESULTS AND DISCUSSION

Figure 2 shows the transesterification reaction using an alkaline catalyst to produce the main product is FAME, some researchers have revealed that the MgO catalyst can provide 91% fatty acid methyl ester (FAME) yield under supercritical conditions (300°C) as well as at high methanol to oil molar ratio (39.6:1) [15].

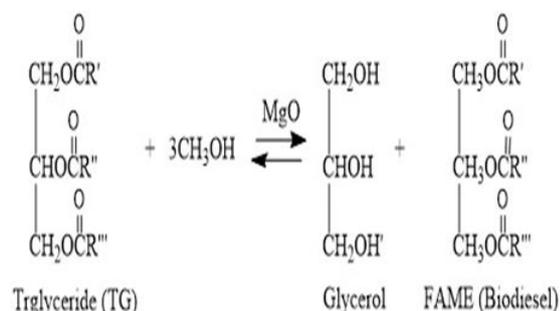


Figure 2. Transesterification reaction between glycerol and methanol, glycerol is a by-product of the reaction.

Figure 3 shows the alkaline catalytic reaction that occurs with RCOOH to produce soap and the use of water as a neutralizer.

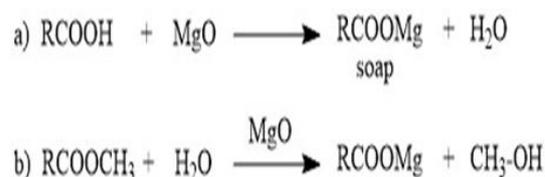


Figure 3. (a) The reaction of an alkaline catalyst with free fatty acids to make soap and water, both undesirable byproducts. (b) Water supports the formation of free fatty acids. Then, it can neutralize the catalyst and produce soap, as in (a)

3.1 Reactor Type

Fluidized bed reactors are widely used in the materials processing industry for processes that require excellent heat and mass transfer between particles and gases. The energy supplied to the fluidized bed usually comes from warm gases that are also fluidizing the bed. The gas distributor is the most important component of the fluidized bed reactor, to provide a uniform distribution of gas to the particles providing stable fluidization. If there is a slight change in gas distribution in the grid zone, it directly affected the quality of fluidization above the grid zone. When the pressure drop of the gas distributor is too small, partial defluidization may occur. However, if the pressure drop is too high, the power consumption increased [19].

Fluidization occurs when small solid particles are suspended in an upward flowing fluid stream. The fluid velocity is sufficient to hold the particles, but not large enough to carry them out of the vessel [20]. The solid particles swirl around the bed rapidly, creating excellent mixing between them. A fluidized material is always a solid and the fluidization medium is a liquid or a gas. The characteristics and behavior of the fluidized bed are: highly dependent on the solid and liquid properties.

Currently two types of fluidized bed reactors have been developed and used mainly by Sasol: circulating fluidized bed (CFB) and fixed fluidized bed (FFB). In the CFB reactor, the fine catalyst particles are attracted by a high-speed gas stream through the riser reactor. The catalyst is separated from the effluent by a cyclone and returned to the reactor inlet. Due to the fluidization problems observed in the CFB reactor, Sasol developed a TBS version, which operates in a bubble regime and is cooled internally by cooling tubes [21].

3.2 Thermodynamics Overview

To determine whether the reaction is exothermic or endothermic, it is necessary to prove it by using the heat of the reaction ($\Delta H^{\circ}f$). The value of $\Delta H^{\circ}f$ for

each component is shown in Table 2.

Table 2. $\Delta H^{\circ}f$ and $\Delta H^{\circ}G$ values for some components

Component	$\Delta H^{\circ}f$ (kJ/mol)	$\Delta G^{\circ}f$ (kJ/mol)
Triglycerides	-672.1	-315.09
CH ₃ OH	-201.2	-166.36
Oleic (C ₁₈ H ₃₄ O ₂)	-764.8	-84.84
Linoleic (C ₁₈ H ₃₂ O ₂)	-424.6	-13.04
Glycerol (C ₃ H ₈ O ₃)	-68.3	118.28

The number of $\Delta H^{\circ}f$ and $\Delta G^{\circ}f$ of the reaction that occurs is calculated to determine whether the reaction is exothermic or endothermic.

$$\begin{aligned} \Delta H^{\circ}f_{\text{reaction}} &= \sum \Delta H^{\circ}f_{\text{product}} - \Delta H^{\circ}f_{\text{reactant}} \quad (1) \\ &= [(\Delta H^{\circ}f_{\text{C}_{18}\text{H}_{34}\text{O}_2}) + (\Delta H^{\circ}f_{\text{C}_{18}\text{H}_{32}\text{O}_2}) + \\ &\quad (\Delta H^{\circ}f_{\text{C}_3\text{H}_8\text{O}_3})] - \\ &\quad [\Delta H^{\circ}f_{\text{Triglycerides}} + (\Delta H^{\circ}f_{\text{CH}_3\text{OH}})] \\ &= [(-764.8) + 3 \times (-424.6) + (-68.3)] - \\ &\quad [-672.1 + 3 \times (-201.2)] \\ &= -831.2 \text{ kJ/mol} \end{aligned}$$

From the value of $\Delta H^{\circ}f$, the reaction obtained from the calculation results is negative, then the transesterification reaction in the reactor is exothermic. The transesterification process is carried out in a fluidized bed reactor at a temperature of 300°C and a pressure of 1 atm.

$$\begin{aligned} \Delta G^{\circ}f_{300\text{K}} &= \sum \Delta G^{\circ}f_{\text{product}} - \sum \Delta G^{\circ}f_{\text{reactant}} \quad (2) \\ &= [(\Delta G^{\circ}f_{\text{C}_{18}\text{H}_{34}\text{O}_2}) + (\Delta G^{\circ}f_{\text{C}_{18}\text{H}_{32}\text{O}_2}) + \\ &\quad (\Delta G^{\circ}f_{\text{C}_3\text{H}_8\text{O}_3})] - \\ &\quad [\Delta G^{\circ}f_{\text{Triglycerides}} + (\Delta G^{\circ}f_{\text{CH}_3\text{OH}})] \\ &= [(-84.84) + (3 \times -13.04) + (118.28)] - \\ &\quad [-315.09 + (3 \times -166.36)] \\ &= 819.85 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \ln K_o &= \frac{\Delta G}{-RT} \quad (3) \\ &= \frac{819.85}{-8.314 \times 300} \\ K_o &= 1.39 \end{aligned}$$

$$\ln \frac{K}{K_o} = -\frac{\Delta H}{R} \times \left(\frac{1}{r} - \frac{1}{r_o} \right) \quad (4)$$

$$\ln \frac{K}{1.39} = -\frac{-831.2}{8.314} \times \left(\frac{1}{573} - \frac{1}{300} \right)$$

$$\frac{K}{1.39} = e^{-0.159}$$

$$K = 1.186$$

The results of the calculations show that the value of K is more than 1, then the equilibrium reaction tends towards the product. The concentration of the product is greater than the concentration of the reactants at equilibrium. The

higher the initial temperature of the reactor, the reaction temperature in the reactor increased.

3.3 Reaction Product Optimization

Optimization of reaction products and reactor model can be assumed as follows:

- The type of reactor used is a three-phase fluidized bed reactor,
- The temperature of the reactor is 300°C,
- Reactor operating system in isothermal condition,
- Nitrogen gas is used as an inert gas for fluidization,
- The raw materials used for biodiesel production are soybean oil, methanol, and MgO catalyst,
- Fatty acids composition of the used soybean oil consists of 90% triglycerides, 7% free fatty acids, and 3% water,
- Bed consists of compartments, namely bubbles, cloud, and emulsion phase,
- Bubble growth occurs along the height of the reactor from the initial diameter to the maximum stable bubble diameter.

IV. CONCLUSIONS

Based on the research that has been done, the reactor design made using a heterogeneous base catalyst MgO in producing FAME products can be used on an industrial scale. The reactor used is a three-phase fluidized bed reactor, which can produce 80,000 tons of product per year at a temperature of 300°C. With the results of thermodynamic calculations, the resulting k value is 1.312 and the reaction $\Delta H^{\circ}f$ is -384.4 kJ/mol, so the transesterification reaction in the reactor is exothermic.

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NOMENCLATURE

k = equilibrium constant

R = ideal gas constant, J/mol-K

T = temperature, K

$\Delta G^{\circ f}$ = standard Gibbs free energy change of
formation, kJ/mol

$\Delta H^{\circ f}$ = standar enthalpy change of formation,
kJ/mol