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Research Article

Optimizing the Yield Product by Changing the Reactor Type for CO2 Hydrogenation in Methanol Synthesis with Process Simulation Software

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Abstract

Hydrogenation is chosen as a process to reduce CO2 in the air, based on its thermodynamic stability. One of the important things to increase the yield product is by using reactor. This study aims to compare two types of reactor, i.e. equilibrium reactor and conversion reactor. In this study, we made two types of processes as the representative for each type of reactor, by using the reaction and kinetic data from reference. As the result, we investigate the yield product result and the energy used. The number of energy used (in kW) in line to total yield product. For the equilibrium reactor, the yield product and energy used in kilowatt are lesser than the conversion reactor, and for conversion reactor is vice versa. Two of the results state that the higher total amount of energy used the higher total yield product. For the future study, this study could be one of the reference, or could be one of the future consideration for choosing exact reactor based on their needs.

Keywords: CO2; Hydrogenation; equilibrium reactor; conversion reactor; methanol

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1. Introduction

In recent times, CO_2 becomes one of the hot topics to talk about, especially with the increasingly widespread campaign about green industry that seeks to reduce CO_2 as a result of industrial combustion. In everyday life, CO_2 is one of the main contributors to greenhouse gases [1]. In the data, the main producer of CO_2 today is the burning of fossil fuels, because after all, 85% of energy is still obtained from fossil fuels [2]. In addition to fossil fuel combustion, eruptions from volcanoes also have an impact on increasing CO_2 levels in the air [3]. CO_2 is certainly a type of gas that has an impact on human health. It is noted that CO_2 is responsible for the environment and humans. For the environment, its presence over time will produce acid rain which is corrosive and erosive. As for health, CO_2 is responsible for symptoms of coughing, wheezing, shortness of breath, and other respiratory problems. In more severe conditions, it can cause respiratory acidosis, decreased lung function, and impaired gas exchange in the lungs [4]. In general, the effect of high levels of CO_2 to human development index could be threatened for human health, life expectancy at birth, cognitive ability of students and reduce the level of human development [5]. Considering its various impacts on life, it is necessary to take steps to reduce the impact of CO_2 emissions by reducing the presence of CO_2 itself in the environment.

CO_2 is physically a gas that colorless, tasteless, odorless, and nonflammable and heavier than air and may accumulate at lower spaces, causing a deficiency of oxygen. Due to its stability and physical properties, one of the processes for

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CO_2 utlization is hydrogenation. Based on [6] hydrogenation is reduction of a substrate (organic or mineral) by addition of hydrogen. The hydrogen involved in hydrogenation process used to come from hyride (H-) or the hydrogen atom (H) accompanied by proton addition. The hydrogenation reactions could be categorized by the source of electron and proton itself. When the (H_2) becomes source of electron and proton, the reaction could be hydrogenation. When another molecule becomes the source of proton and electron, the reaction will be known as transfer hydrogenation or dehydrogenation [6].

The hydrogenation of CO_2 is kind of challenging due to the thermal stability of CO_2, and making low conversions of reaction, some of the progress has been made towards converting CO_2 to single carbon (C1) products (e.g., formic acid, carbon monoxide (CO), methane, and methanol) through the direct hydrogen reduction or hydrothermal-chemical reduction in water [7].

After the process of hydrogenation, methanol (CH_3OH) comes out as the result of CO_2 hydrogenation. The reaction simply occurs at 483.15 °K as:

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H_r = -49.5 \text{ kJ/mol}, \Delta G_r = 3.48 \text{ kJ/mol} \quad (1)$$

For the addition, the reaction of methanol production usually accompanied by the production of car bon monoxide (CO), also known as the reverse-water-gas-shift (RWGS) reaction 623.15 °K:

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad \Delta H_r = 41.2 \text{ kJ/mol}, \Delta G_r = 28.6 \text{ kJ/mol} \quad (2)$$

In the production of methanol from CO_2 hydrogenation, numerous studies have appeared to increase the conversion of CO_2 to methanol from hydrogenation [9-12]. Also for the industrial application, hydrogenation (in general, different compound) becomes the essential step for production [13,14] .

In industrial field, to increase and help the process, reactor will be one of the essential thing in production system. As the definition, based on Awogbemi and Kallon [15] reactor is a device or vessel with compartments where chemical reactions take place for the transformation of raw materials into desired products under specific and predetermined conditions. Still from the same source, as the terms, a proper reactor should include mechanisms or facilities for injection of feedstock and other reagents, providing sufficient residence time for the chemical reaction to take place, and discharging the products. There should be facilities for heat addition and heat removal, safe operation and maintenance, and effective controls to ensure operational safety, effectiveness, and acceptable productivity levels. In other opinion, Evelyn Lee [16], stated that the use of reactor has proven as the step for increasing the methanol conversion result. Reactors play a central role in converting raw materials into desired products by facilitating chemical reactions under specific conditions. Effective reactor design ensures optimal reaction rates, high product yields, and efficient energy utilization. Based on the important role of the reactor, it automatically makes the reactor design something that needs to be considered. The reactor architecture directly impacts performance by controlling the internal resistance, which in turn governs the maximum current density and reactant productivity [17]. From other opinion, the reactor designs have a significant change in the geometry entrance and outlet area without any change in the height and volume of the thermochemical reactor [18]. There are so much way to design the reactor based on their needs, such as the temperature and feeding ratio [19], or the geometry of the reactor [18]. One of the innovation of reactor design in process is the use of conversion reactor and equilibrium reactor. Based on Kawale *et al.* [20], there are two types of reactor, conversion reactor and equilibrium reactor. As the definition, an equilibrium reactor is a vessel that is modelling an equilibrium reaction. The reactor outflow is in a state of chemical and physical equilibrium. The reaction set can contain an unlimited number of equilibrium reactions, which are completed simultaneously or sequentially. For this kind of reaction, the quantity of each component at equilibrium is related to the equilibrium constant, on the other hand, conversion reactor is the reactor which the reaction is performed is referred to as the conversion reactor. The user only able to attach reaction sets that contains conversion reactions. The stoichiometry of all reactions and the conversion of the limiting reactants. This reactor calculates the composition of the outflow [20]. For the example of equilibrium use is Varandas *et al.* [21] for the steam methane reforming, and for the conversion reactor such as Makkawi *et al.* [22] for the biomass conversion reactor. In this paper study, we aims to compare the impact of using equilibrium reactor and conversion reactor based on the yield product and energy used during process. The change form equilibrium reactor to conversion reactor based on one of the reason from Agustriyanto *et al.* [23], the conversion reactor are able to increase the coversion and simplify the reaction.

To simplify the works of comparing reactor type, we use a process simulator. Based on Bartolome and Gerven [24], the definition of process simulation are tools widely used by chemical engineering researchers, starting to be functional from the early 1960s. One of the process simulation that usually used by process engineer is HYSYS v.11 that already applied in this paper study.

Based on process simulation of Borisut *et al.* [25], the reactor used was the equilibrium reactor in series, the conversion result in percent until 94%. From that conversion, in this study, we decided to make an innovation in the form of changing the equilibrium reactor into conversion reactor until the conversion result is obtained higher, as well as comparing the energy requirements used (in kW) with the amount of yield product (in per cent) that can be produced. In the comparison process, HYSYS v.11 simulation software is used to simulate the equilibrium reactor and conversion reactor processes, so that data is obtained between energy requirements and product yields for each type of reactor.

2. Methods

For comparison, first, using the equilibrium reactor, similar to reference Borisut *et al.* [25], with the process data following the reference. Second, as the point of the test, made the simulation using the conversion reactor, with the process data similar to previous simulation. After making two simulations, we compare the product yield result and the energy used by two of the processes.

As the detail step making two simulations, the carbon dioxide hydrogenation in methanol production was simulated using the ASPEN HYSYS v.11 process simulator with the Peng-Robinson property package [25].

Reaction 1: Reverse water-gas shift reaction

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad (3)$$

R

eaction 2: Methanol synthesis from carbon monoxide and hydrogen

$$CO + 2H_2 \leftrightarrow CH_3OH \quad (4)$$

Reaction 3: Methanol synthesis directly from carbon dioxide and hydrogen

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad (5)$$

These following steps make up the hydrogenation process that converts carbon dioxide to methanol. First, a mix of 3000 kg.mole/h of hydrogen at 25 °C and 1000 kg.mole/h of carbon dioxide at 40 °C are fed into a mixer with 20 bar pressure. The feed stream was then compressed to 71.9 bar. After being compressed, the stream then went into the heater to increase the temperature to 35 °C.

The first section of the methanol production is the methanol production from the reactant in reactor (equilibrium reactor for the first simulation and conversion reactor for the second simulation). The heated feed enters the conversion reactor. The conversion reactor is set to 71.9 bar and a high temperature of 300 °C. In this reactor the hydrogenation of carbon dioxide occurs. Some catalyst used in this reaction to help fasten the reaction. Due to the high pressure and temperature of the reaction, a copper-based catalyst such as Cu-ZnO/Al_2O_3 was performed in this reaction.

The gas product with a high temperature from the conversion reactor, then went into the heat exchanger in order to decrease the temperature until it reaches a temperature of 40 °C. In decreasing the temperature, the methanol product is separated as liquid. As for the vapor, it fed back to be recycled. The recycle stream then went back to the mixer to combine with the reactant feed stream.

The methanol then went into a purification process into two distillation towers. In the first distillation tower, a light component (hydrogen, carbon dioxide, and carbon monoxide) is separated from the methanol mixture. This distillation tower produces top product of light component, and bottom product of the methanol and water mixture. The stream then went into the second distillation tower which separates the pure methanol from water. This distillation tower resulted in pure methanol as the product and water as the by-product.

3. Results and Discussion

The modification of the type of reactor used was carried out to optimize the conversion of the carbon dioxide hydrogenation process into methanol. The reactor was changed from an equilibrium reactor to a conversion reactor. The final conversion only reaches 94% when using the equilibrium reactor. Meanwhile, the final conversion reaches 99% when the conversion reactor is used. The conversion value can be determined using the following formula.

$$\text{Conversion} = \frac{\text{Reacted ethylbenzene}}{\text{Incoming ethylbenzen}} \times 100\% \quad (6)$$

Heat exchanger are designed to transfer heat effectively from one fluid to another without changing the nature or phase of the fluid, because the process designed has a lot of high temperature

Table 1. Reactor's stream

Component	Molar Flow (kg.mole/h)	
	Input Feed Reactor	Output Feed Reactor
CO_2	1000	0

steam that is wasted, it would be better if in this process using a heat exchanger rather than a heater because it can save energy by energy consumption of 2.625e+007 kJ/h.

To separate methanol, which is the reactor's product, from the other chemicals still within (such as hydrogen gas, carbon monoxide), a liquid-liquid vapor separator is used. The LLV in use functions at 50 °C and 60 bar of pressure. liquid products such as methanol and water are obtained from the bottom of the separator, while a mixture of gases such as carbon monoxide, carbon dioxide, and hydrogen exit at the top of the reactor. Carbon monoxide, carbon dioxide, and hydrogen gases are recycled back to the heater to increase methanol production.

$$\Delta G^{\circ}_{r,298K} = \Sigma\Delta G^{\circ}_{f,298K,product} - \Sigma\Delta G^{\circ}_{f,298K,reactant} \quad (7)$$

$$\Delta G^{\circ}_{r,298K} = \Sigma\Delta G^{\circ}_{f,298K,CH_3OH} - (\Delta G^{\circ}_{f,298K,CO} + 2\Delta G^{\circ}_{f,298K,H_2} \quad (8)$$

$$\Delta G^{\circ}_{r,298K} = -90.6\ kJ/mol$$

$$\Delta G^{\circ}_{r,298K} = -RT \ln K\ 298 \quad (9)$$

$$\ln K_{298} = -\frac{\Delta G^{\circ}_{r,298K}}{RT} \quad (10)$$

$$\ln K_{298} = -\frac{-29700}{8.314\ x\ 298} \quad (11)$$

$$\ln K_{298} = -\frac{-29700}{2478.772} = 11.981$$

$$K_{298} = \exp(\ln K_{298})$$

$$K_{298} = \exp(11.981) \approx 1.61\ \times 10^5$$

Compared to equilibrium reactors, conversion reactors allow for higher methanol production. This increase is due to the ability of conversion reactors to maintain reaction conditions that favor the forward reaction of methanol synthesis, especially under optimized pressure and temperature conditions. In contrast, the thermodynamic limitations often encountered in equilibrium reactors result in lower methanol yields.

In equilibrium reactors, reactions proceed until thermodynamic equilibrium is reached, potentially limiting product yield. Conversion reactors, however, operate based on predefined reactant conversion rates, allowing for enhanced control over reaction extents and improved methanol yields. This approach aligns with findings that emphasize the importance of reactor design in optimizing chemical processes.

After simulation, the results are shown in the figure and table. Figure 1 shows the process flow diagram of methanol synthesis using Visio software after modifying. Figure 2. shows the process flow diagram of methanol synthesis before the reactor type change, which still uses the equilibrium reactor. Figure 3. shows the process flow diagram with the change in reactor type to a conversion reactor. Figures 2 and 3 do not reveal any significant differences before and after the innovation, but the energy used does, which is shown in Table 2. In line to the yield product, which is shown in Table 3. Tables 2 and 3 show the significant difference between the use of equilibrium reactors and conversion reactors. In terms of images, Figure 2 is similar to Figure 3. However, there is a difference in the reactor marker where Figure 2 showing the symbol 'E' for equilibrium and Figure 3 showing the symbol 'C'

Table 2. Comparison of reactor energy consumption.

Reactor	Energy (kW)
Equilibrium	6739.8
Conversion	907.3

Table 3. Comparison of reactor yield product

Reactor	Total Yield Product (%)
Equilibrium	94
Conversion	99

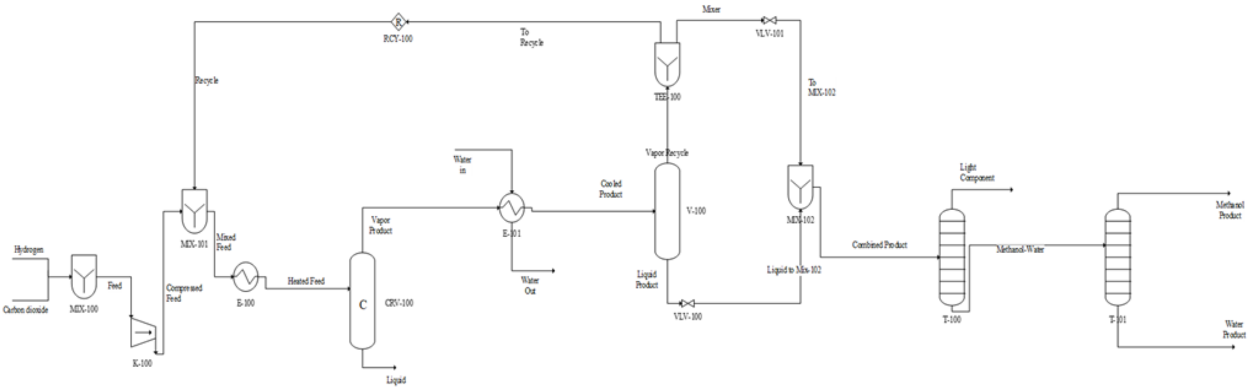

Figure 1. Process flow diagram for the production process of methanol after modification

for conversion. The big difference will appeared when we examine about the energy used and yield product. The conversion reactor has a higher amount of energy used, as shown in Table 2, which is 907.3 kW, while the equilibrium reactor has a total energy used of 6739.8 kW. This is proportional to the yield product produced, according to Table 3. where the yield of the conversion reactor is 99%, higher, compared to the yield of the equilibrium reactor of 94%.

4. Conclusions

The presence of a reactor is essential for CO_2 hydrogenation process for methanol synthesis applications. The type of reactor certainly determines the hydrogenation conversion yield. In this study, it has been shown that the type of reactor clearly affects the difference in hydrogenation yield and the total amount of energy used (in kW). With the same kinetic data, but different reactors can influence the hydrogenation yield and total amount of energy used. For the equilibrium reactor from previous study had conversion 94%, and for the conversion reactor from our simulation have conversion 99%, for the total energy used (in kW), equilibrium reactor has 6739.8 and the conversion reactor has 907.3. The two results state that the higher total amount of energy used, the higher the yield product. This can certainly be a future consideration for the selection of reactor types and the use of process simulations.

CRediT Author Statement

A.D.K. Zahra: Writing, Review and Editing, Resource Investigation, Formatter, Validation; N.S. Rabbani: Writing, Review and Editing, Methodology; M.N. Ramadani: Writing, Visualization, Simulation, Validation; Y.Z. Muafi: Writing, Visualization, Simulation, Data Curation. All authors have read and agreed to the published version of the manuscript.

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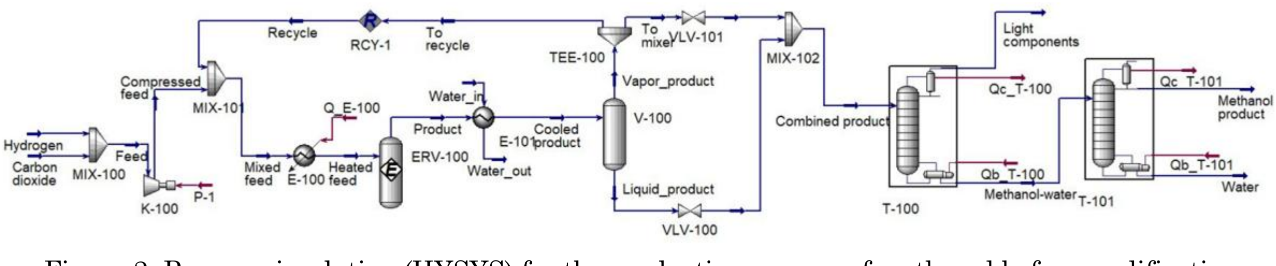

Figure 2. Process simulation (HYSYS) for the production process of methanol before modification

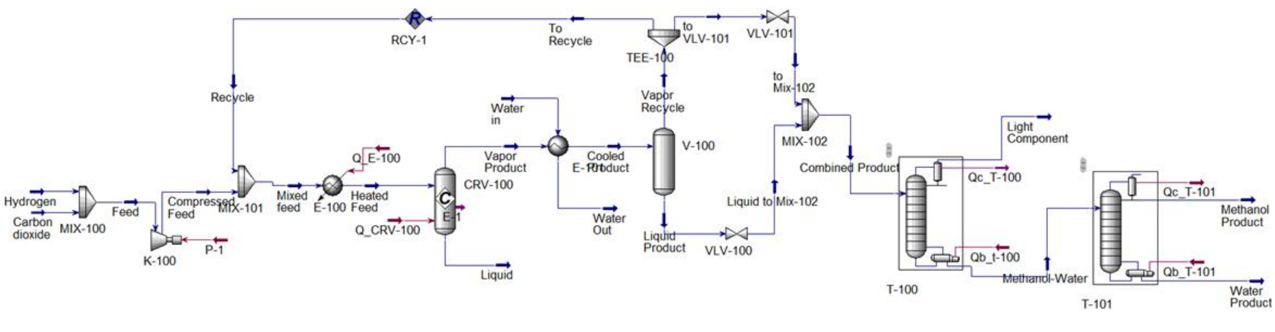

Figure 3. Process simulation (HYSYS) for production process of methanol after modification

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