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Research Article

Optimizing Methanol Production Yield through Carbon Dioxide Hydrogenation Process with Continuous Stirred Tank Reactor and Transition from Partial to Total Condenser in Distillation

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Abstract

Methanol is a chemical product that is widely applied in the chemical industry. The methanol production process from carbon dioxide and hydrogen uses a hydrogenation process with a continuous stirred tank reactor (CSTR) under controlled thermodynamic and kinetic conditions. The process was modified by replacing the Gibbs reactor with a Continuous Stirred Tank Reactor (CSTR), adding temperature and pressure regulation, and a compressor. This study aims to increase the product yield obtained from the modification results and mass efficiency. Based on the experimental results, it can be concluded that the modified design is quite effective compared to before modification, because it increases the methanol product yield from 44.54% to 99.78%.

Keywords: Methanol; carbon dioxide; hydrogenation; HYSYS simulation; yield optimization

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1. Introduction

Methanol is a versatile chemical that can be used in various fields, including chemical production, pharmaceuticals, and fuel production [1]. Globally, methanol production is increasing year on year. China, the United States, Europe, and the Middle East are the major methanol the main methanol producing regions [2]. At present, methanol is mainly produced by coal gasification, natural gas reforming and other processes [3]. Methanol production by CO_2 captured from flue gas from fossil fuel power plants and by H_2 produced by electrolysis of water using renewable energy is expected to be one of the most promising technologies for emission reduction in the future [4]. The process of methanol synthesis via CO_2 hydrogenation is well known and studies on the reaction mechanism and catalysts have been conducted to investigate the possibility to improve the conversion and efficiency of the system [5].

CO_2 utilization is a promising strategy because it is converted into useful chemicals such as methanol that benefit human life while reducing the CO_2 in the atmosphere. Conversion of CO_2 to methanol is a more attractive utilization strategy because methanol can be further converted into useful chemicals (formaldehyde, acetic acid, etc.) and fuels (olefins, gasoline, etc.) [6]. This article aims to increase yield of process product by modification of process in term of mass efficiency.

2. Methods

2.1 Process Simulator

Recently, many researchers and engineers are developing models for physical, chemical, and

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biological systems using process simulators to minimize experimental procedures. Process models are critical in analyzing system behavior, measuring performance, and examining the impact of various operating parameters [7]. Process simulators are tools widely used by chemical engineering researchers. Starting to be functional from the early 1960s they have been shown to replicate the real behaviour of chemical plants and are a valuable tool not only for process design, but also for proces optimization, tuning of the control loops or training of operators. Of the many chemical engineering programs available such as Aspen Plus, Aspen Hysys, UniSim, CHEMCAD, PRO/II or DWSim, Aspen Hysys was chosen for two reasons: first, its high popularity among researchers, and second, its high its highularity among researchers, and secondly, the open access of the automation server [8].

Nowadays, as like for the steady state design and rating, the simulation software are extensively applied in control structure design and analysis. Among the process software, Aspen HYSYS is widely accepted in both industry and academia for wide areas of steady state and dynamic simulation, process design, performance modeling and optimization [9]. Aspen HYSYS is an equation-oriented software that operates on the basis of mass-energy balance and phase equilibrium database to analyze the effects of diverse process parameters. It is an important software for chemical process design [7]. It supports many of process calculus including mass and energy balances, thermodynamics, reaction kinetics etc. The user can also customize the Aspen-HYSYS for supplementary tasks in two general frames of “extension” and “automation”. The extensions are the customized property packages, unit operations or reaction kinetics created or modified by the user. The automation enables the HYSYS or its related objects to serve within other third-party tools such as Microsoft visual basic, C++, etc. [9]. HYSYS additionally provides an Internal Macro Engine named WinWrap Basic that supports the same syntax as Microsoft Visual Basic. With this engine, the user can automate the desired tasks without the need for another program [10].

2.2 Basic Process Flow Diagram

The flow diagram methanol synthesis is presented in Figure 1 [11]. The feed consists of carbon dioxide gas and pure hydrogen gas. The feed enters into MIX-100 to provide the possibility to adjust the feed gas ratio. Next, stream 1 is compressed in K-102 and sent to MIX-101 where stream 2 is mixed with REC recycle stream from RCY-1. After compression, the gas is heated or cooled before the gas enters GBR-100. The gases are converted to methanol. Stream 5 is cooled in cooler E-101, then enters V-100, a gas-liquid separator. TEE-100 splits flow B1 into co2 purge stream, while flow B2A goes to RCY-1 and returns to MIX-101 along with the feed gas. Stream B2 is depressurized and enters the T-100 distillation column where methanol and water are separated. The remaining gas exits in the Gas stream.

2.3 Thermodynamics Consideration

Thermodynamic analysis is utilized to ascertain the characteristics and direction of reactions, specifically whether they are exothermic or endothermic, as well as reversible or irreversible. In the selected process for this simulation, a single reactor is employed where the methanol dehydration process takes place [12]. The main reaction within the reactor (Equation (2)) features the values of $\Delta H^{o}_{f,298K}$ for each component and $\Delta H^{o}_{r,298K}$ at a temperature of 298 K, which can be found in Table 1 [13]. The value of $\Delta H^{o}_{r,298K}$ for the reaction is obtained as follows:

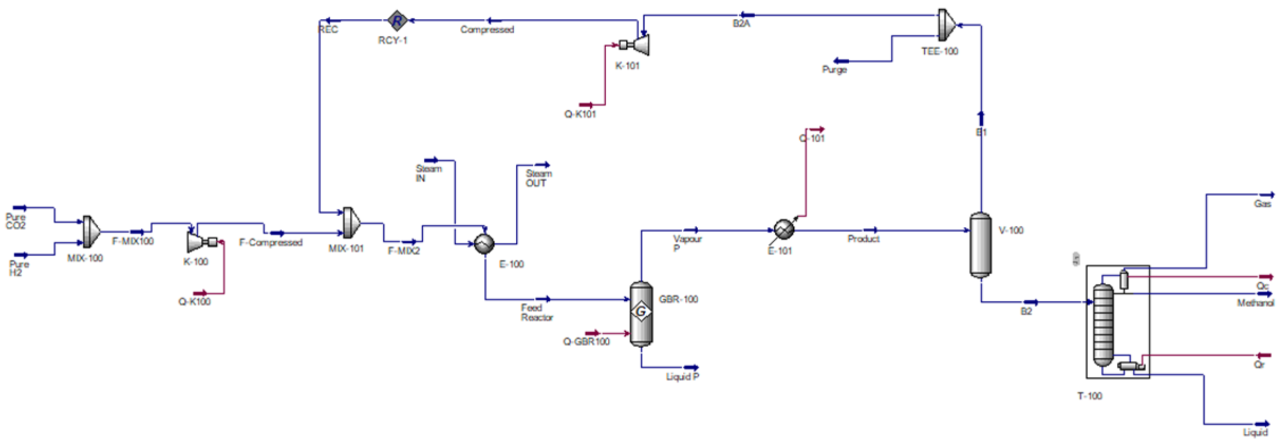

Figure 1. Aspen HYSYS simulation of basic process

$$\Delta H^o_{r,298K} = \sum \Delta H^o_{f,298K,product} - \sum \Delta H^o_{f,298K,reactant}$$
$$\Delta H^o_{r,298K} = (\Delta H^o_{f,298K,CH_3OH} + \Delta H^o_{f,298K,H_2O}) - (\Delta H^o_{f,298K,CO_2} + 3\Delta H^o_{f,298K,H_2O})$$
$$\Delta H^o_{r,298K} = (\text{-201.17} + \text{-241.83 (kJ/mol)}) - (\text{-393.50} - 3(0) \text{ (kJ/mol)}$$
$$\Delta H^o_{r,298K} = \text{-49.50 kJ/mol}$$

Based on the calculations, we get value $\Delta H^o_{r,298K} = -49.50$ kJ/mol with negative value that the reaction is exothermic.

The value $\Delta G^o_{f,298K}$ of each component at the temperature 298 K can be seen in Table 2. The $\Delta G^o_{f,298K}$ of main reaction is obtained as follow:

$$\Delta G^o_{r,298K} = \sum \Delta G^o_{f,298K,product} - \sum \Delta G^o_{f,298K,reactant}$$
$$\Delta G^o_{r,298K} = (\Delta G^o_{f,298K,CH_3OH} + \Delta G^o_{f,298K,H_2O}) - (\Delta G^o_{f,298K,CO_2} + 3\Delta G^o_{f,298K,H_2O})$$
$$\Delta G^o_{r,298K} = (\text{-162.51} + \text{-228.59 (kJ/mol)}) - (\text{-394.40} - 3(0) \text{ (kJ/mol)})$$
$$\Delta G^o_{r,298K} = \text{3.30 kJ/mol}$$

The magnitude of equilibrium constant (*K*) at 298 K can be calculated as:

$$\ln K_{298} = -\Delta G^o_{r,298K}/RT$$
$$\ln K_{298} = -\text{3.30 kJ/mol}/(\text{8.314 kJ/mol})(\text{298 K})$$
$$\ln K_{298} = \text{-0.00133}$$
$$K_{298} = 0.99967$$

At reactor temperature of 268.2 °C (541.4 K) the magnitude of the equilibrium constant (*K*) can be calculated as follow:

$$\ln K_{541.4}/K_{298} = \Delta H^o_{r,298K}/R \times \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)$$
$$\ln K_{541.4}/0.99967 = 49.50 \text{ (kJ/mol)}/(8.314 \text{ kJ/mol}) \times \left(\frac{1}{541.4} - \frac{1}{298}\right)$$
$$K_{541.4} = 0.990727$$

Based on the calculations we have done, we get *K* at 541.4 K = 0.990727 and the reaction occurs reversibly.

2.4 Modification of Gibbs Reactor to CSTR Reactor

Every industry must always strive to improve efficiency and effectiveness in order to survive in the market. This relates to the production process and production speed [14]. Through a good production system and a controlled process, the Company can manage and continuously improve the process to minimize waste during the process. Therefore, the company must be able to maintain stability and correct defects in its production process. Waste can be defined as all work activities that do not add value to the process that converts inputs into outputs along the value stream. Yield is the ratio between output and production input and represents the

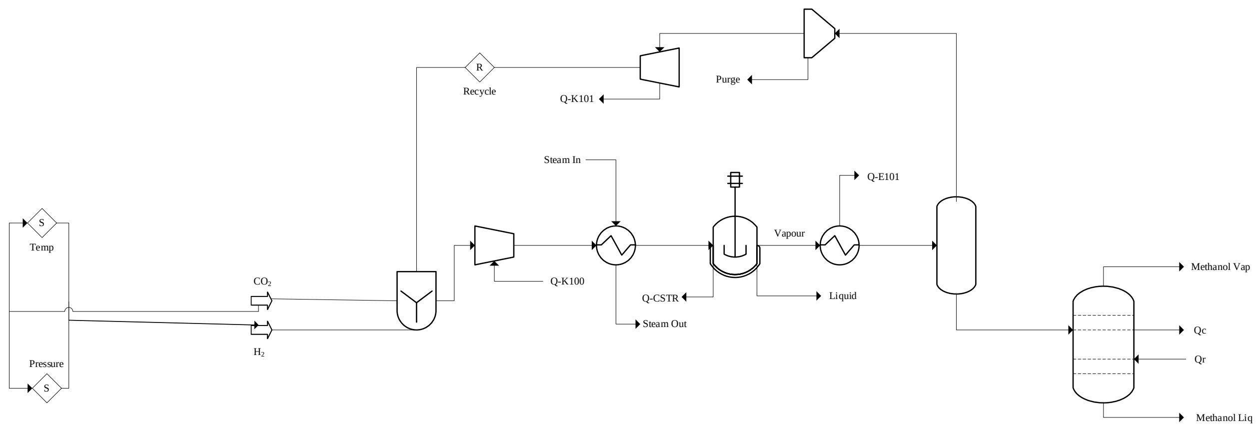

Figure 2. Process Flow Diagram (PFD) of modified proces

Table 1. Enthalphy formation of components and enthalphy of reaction of the main

Compounds	Molecular Formula	$\Delta H^o_{f,298K}$(kJ/mol)
Methanol	CH_3OH	-201.17
Water	H_2O	-241.83
Carbon Dioxide	CO_2	-393.50
Hydrogen	H_2	0

Table 2. Gibbs' free energy formation of components on the reactor

Compounds	Molecular Formula	$\Delta G^o_{f,298K}$(kJ/mol)
Methanol	CH_3OH	-162.51
Water	H_2O	-228.59
Carbon Dioxide	CO_2	-394.40
Hydrogen	H_2	0

value of production efficiency. The definition of industrial efficiency is the ability of an industry to produce maximum output with a certain amount of input, or the ability of an industry to produce a certain amount of output with a minimum amount of input. If the power ratio is higher, it is said that the efficiency is higher. Efficiency can be described as the maximum utilization of inputs in producing output. Yield is closely related to the efficiency of a factory process, so the modification we will do is to increase the yield obtained [15].

In this simulation, the Gibbs reactor is used for calculating Gibbs free energy minimization for a reaction and its products based on reaction equilibrium. However, in practical situations where the reaction time is short, equilibrium may not be achieved, resulting in lower than expected methanol production. To address this, we propose using a continuous stirred tank reactor (CSTR) to gain better insights into reaction kinetics, which include reaction speed, residence time, and the impact of pressure and temperature on the reaction [16].

A CSTR allows us to study the reaction kinetics by employing the power law model for reaction rates. This model is expressed as $-r_A = kC_A^aC_B^b$, where $-r_A$ is the rate of disappearance of reactant A, C_A and C_B are the concentrations of reactants A and B, respectively, and a and b are the reaction orders. The rate constant k is temperature-dependent and follows the Arrhenius equation: $k = Ae^{E/RT}$, where A is the pre-exponential factor, E is the activation energy, R is the universal gas constant, and T is the temperature [12]. This detailed kinetic analysis allows for optimizing reaction conditions to increase yield. By modifying the reactor to a CSTR, we can better control these variables and potentially increase the yield of methanol, although this may require more energy input [17].

In addition to the use of a CSTR reactor, the partial distillation column used was modified to total distillation. In the total distillation process, the use of a total condenser is very important to achieve optimal separation efficiency [18]. The total condenser serves to condense all of the vapor lifted from the top of the distillation column, without any of the vapor being wasted, thus ensuring that all of the more volatile components are fully condensed and separated. This makes the use of total distillation more efficient [19].

2.4.1 Reaction mechanism

The actual chemistry of CO_2 hydrogenation involves three main equilibriumreactions (A, B and C) leaing to methanol and water:

$$CO + 2H_2 \leftrightharpoons CH_3OH \quad \Delta H_{298K} = -90.64\ \text{kJ/mol} \quad (1)$$
$$CO_2 + 3H_2 \leftrightharpoons CH_3OH + H_2O \quad \Delta H_{298K} = -49.50\ \text{kJ/mol} \quad (2)$$
$$CO + H_2O \leftrightharpoons CO_2 + H_2 \quad \Delta H_{298K} = -41\ \text{kJ/mol} \quad (3)$$

In an exothermic reaction, energy is released, which results in an increase in the temperature. According to Le Chatelier's principle, the equilibrium will shift towards the reactants.

2.4.2 Operating Conditions

Methanol synthesis produce methanol with a purity 99 wt%. Methanol synthesis is enhanced by low temperature and high pressure, 200 °C and 100 bar are selected. The feed is set to 200 kmol/h. The feed gas composition for methanol synthesis is taken from experiments and simulations conducted at the University of South-Eastern Norway, and the ideal ratio is used for comparison. For the simulation, N_2, H_2O, and CH_4 gases are not included. A recirculation rate of 1100 kmol/h is used in the simulation.

2.4.3 Raw Materials

The feed consists of carbon dioxide gas and pure hydrogen gas. The feed enters into MIX-100 to provide the possibility to adjust the feed gas ratio. Next, stream 1 is compressed in K-102 and sent to MIX-101. Carbon dioxide enters at a temperature of 41 °C with a pressure of 42.5 bar. Where the incoming hydrogen has the same conditions as carbon dioxide.

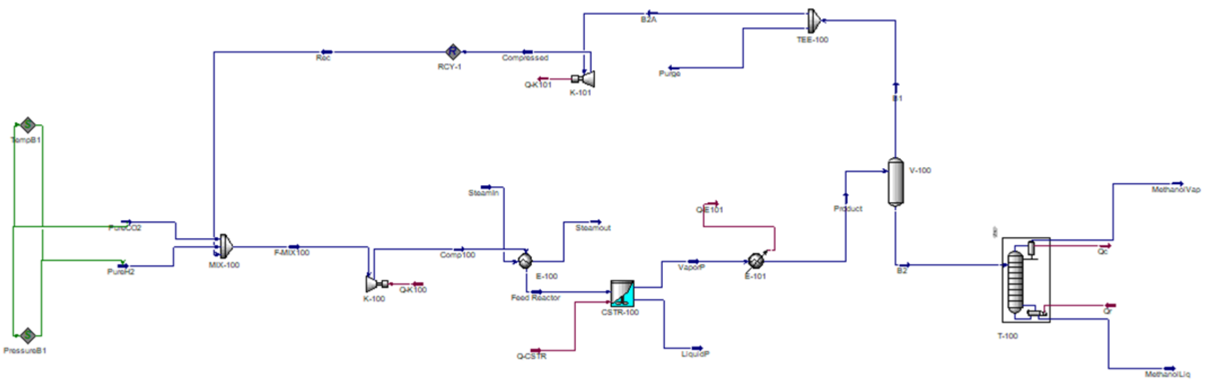

Figure 3. Aspen HYSYS simulation of the modified process

3. Result and Discussion

3.1 Basic Process Flow Diagram and Modification

The design capacity of the industrial methanol production device from a factory is 650 metric tons of methanol per year. The Peng-Robinson-Trukhanov-Wang-Uzoglu (PR-TWU) equation-of-state is used to determine the thermodynamic properties in this study. Oil, gas, and petrochemical applications use the PR-TWU model because of its improved phase behavior predictions and enhanced computational stability for systems with highly non-ideal behavior. The PR-TWU model is particularly advantageous for systems with polar components and hydrogen bonding, providing more accurate predictions of liquid densities and critical properties. This system efficiently and reliably computes solutions for a majority of single-phase, two-phase, and three-phase systems with rigorous precision. The PR-TWU model is more accurate for real gases, making it a suitable choice for complex industrial applications.

The basic process flow diagram was taken from [11]. Hydrogenation reaction is carried in a Gibbs reactor. The Gibbs Reactor of Aspen HYSYS can work solely as a separator, a reactor that minimizes the Gibbs free energy without an attached reaction set or as a reactor using equilibrium reactions. When a reaction set is attached, the stoichiometry involved in the reactions is used in the Gibbs Reactor. Pure hydrogen and pure CO_2.

It can be seen in Figure 2 and Figure 3, where pure hydrogen and pure CO_2 are introduced into a mixer to homogenize the mixture, which is then compressed to a pressure of 4500 kPa. The mixture is then heated to a temperature of 250 °C before being fed into the reactor. The gas is then converted into methanol according to the reactions in Equations (1), (2), and (3). The resulting product is then cooled in a cooler to a temperature of 21 °C. The product is then separated in a separator. The liquid obtained from the separator is purified in a distillation column with a total condenser to obtain methanol at a rate of 22,000 tons per year. Meanwhile, the top product from the separator, in the form of gas, undergoes separation of CO_2 and is compressed to a pressure of 4190 kPa. The compressed gas is then fed back into the mixer.

Table 3. Yield of methanol production before and after modification

Process	Methanol yield (%)
Before modification	44.54
After modification	99.78

3.2 Optimization of Product Yield by Reactor Modification

In this study, the yield unit of the methanol production process was modified by changing the type of reactor from a gibbs reactor to a CSTR reactor [20]. Changing simulations with a continuous stirred tank reactor (CSTR), which requires reaction kinetics, will provide better insight into the reaction speed, residence time, and pressure and temperature that affect the reaction. In CSTR catalytic reactions can also be studied. By modifying this reactor (Figures 2 and 3, the yield produced will increase although the energy required will also increase. The differences in yields produced could be seen in Table 3. In addition to the use of a cstr reactor, the partial distillation column used was modified to total distillation. In the total distillation process, the use of a total condenser is very important to achieve optimal separation efficiency. The total condenser serves to condense all of the vapor lifted from the top of the distillation column, without any of the vapor being wasted, thus ensuring that all of the more volatile components are fully condensed and separated. This makes the use of total distillation more efficient.

4. Conclusion

Methanol production process modification is carried out to produce higher yields. the modification process is carried out by replacing the gibbs reactor with a Continous Stirred Tank Reactor (CSTR), adding temperature and pressure sets, and compressors. Methanol yield with hydrogenation process has increased from 44.54% to 99.78%. Based on the consideration of these various aspects and the objectives of the study, the modified process proved to be more effective and efficient than the basic process. Thus, the plant can minimize by-products, optimize raw materials, and increase production yield.

CRedit Author Statement

Authors contributions: Verisna, C.W : Conceptualization, Methodology, Software, Validation, Formal analysis, Writing-Original draft, Visualization; Lissa'adah, M. : Conceptualization, Validation, Methodology, Formal analysis, Writing, Visualization; Nursatitah, N. : Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Writing, Visualization; Aulia, Z. : Conceptualization, Validation, Methodology, Formal analysis, Writing, Visualization. All authors have read and agreed to the published version of the manuscript.

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