SIMULATION OF METHANOL PRODUCTION PROCESS FROM SYNGAS USING UNISIM DESIGN SOFTWARE

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Abstract

In this study, simulation of a synthesized methanol process from syngas using UniSim Design R470 is performed to analyze the effects of operating parameters on the product purity. The production line consists of two key units known as methanol reactor unit and by-product separation unit. The kinetics model for the reforming step is adopted from literature in the form of heterogeneous catalytic reactions using $Cu/ZnO/Al_2O_3$ catalyst for the simulation of the plug-flow reactor in the process. Numerical results obtained from the simulation generally show that the production rate and its purity are affected by three key factors known as recycle ratio, reaction temperature and pressure. Based on the parameter analysis, the effective operating condition is found at recycle ratio of 0,8 in which reaction temperature and pressure are kept in the range of 180-200^oC and 4-5 MPa, respectively. At this operating condition, purity of the synthesized methanol is higher than 99,9% which can be used as clean fuel, solvent.

Keywords: *Methanol synthesis; simulation; UniSim Design; syngas.*

1. Introduction

Methanol is known as “wood alcohol” because it is one of the byproducts of the wood distillation process. Methanol is often used widely for various industrial purposes such as biofuel, solvents and synthesis of other chemicals. Importantly, methanol is also known as an environmental-friendly material due to its biodegradable feature. Due to its eco-friendly properties and wide application, methanol has been produced on a global scale as in Asia, Europe, America, Africa, the Middle East and more other places [1]. Up to now, hundreds of methanol plants worldwide have been built with the production capacity of nearly 90 million metric tons per year, which is one of the most important commercial chemical products in the world. The global methanol industry has also been creating more jobs around the world and billion dollars in economic activity each year [2]. In 1923, the first commercial process was invented by Badische Anilin and Soda Fabrik (BASF) for methanol production, this synthesis process was then continually developed further by the scientific and technological corporations [3]. Nowadays, methanol is primarily produced from synthesis gas by low-pressure technologies [1-5].

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Currently, the industrial methanol production process comprises of three main steps: the first is to prepare the syngas flow containing H_2, CO_2, CO and steam. In the next step, methanol is syntonized from the syngas stream in a heterogeneous catalytic reactor. This step can be conducted in different technologies for the desired application and techno-economic performance. The last step is often carried out by distillation technique to obtain the desired purity of methanol product [1, 2].

At present, the simulation software is used in design calculations and optimization for chemical engineering processes. In this article, we used the UniSim Design R470 software to simulate the methanol production process from the syngas stream by using hypothetical conditions and supposition reactors. This simulation will contribute to reducing experimental costs pilot scale. In this research, theories about kinetics and modeling for the methanol synthesis process reviewed by referring to the literature [2-9]. The simulation process has used models from previous researches and improving to fit into this study. This simulation software used to assess the performance of the process in steady-state due to the general convention on the reaction mechanism is not uniform among the references so the evaluation of the reliability of the results will be reported by further researches.

2. Experimental

The process of producing methanol is simulated by Simulation software UniSim Design R470. This program provides highly accurate results that made it become one of the most effective software simulators today. It is equipped with a robust thermodynamic database library that allows it to calculate the physical parameters of the phase, calculated the heat transfer and mass transfer processes of the chemical reaction process. The software UniSim Design R470 allows the calculation of process output if input parameters such as temperature, pressure, flow, and material composition are provided.

2.1. Process description

The methanol production process included three main stages [1, 3]:

- The first stage is the production of syngas flow containing H_2, CO_2, CO and steam.

- In the next stage, transform of syngas into the raw methanol product.

- The last stage is distillation to get the purity methanol product.

The simplified block diagram Methanol synthesis is given in the Fig. 1 below:

Firstly, the syngas flows are mixed with the recycle stream and compressed to the required pressure. After that, the mixed feed current is passed through the heat

exchanger to reach required temperature before entering the reactor. The product obtained from the reactor was cooled and transported to the separator. The gaseous phase at the top of the separator tower is recirculated to mix with the original syngas stream, meanwhile, the liquid phase at the bottom of the separator tower is led to the distillation system to separate by-products from methanol. Finally, the methanol is stored in the tank.

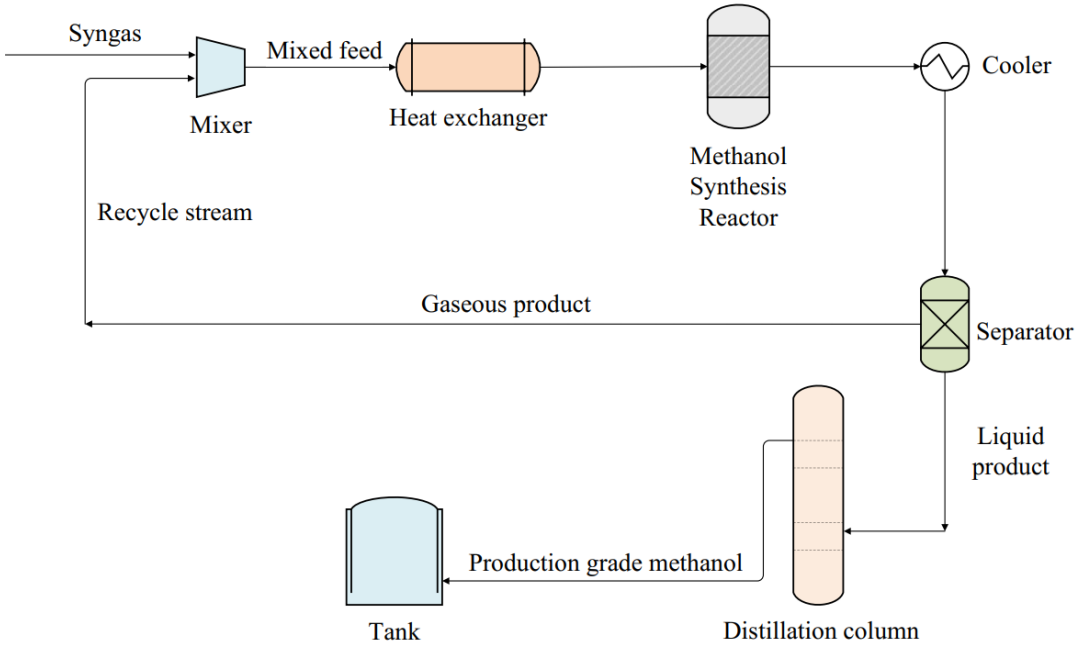

Fig. 1. Process block diagram of methanol production.

2.2. Modeling and simulation

Nowadays, industrial methanol synthesis catalysts is known to contain composition Cu metal, which is as the chemically active agent and Al_2O_3 to disperse Cu nanoparticles as well as ZnO to help Cu in making the methanol product. Besides, metals are often used as additional promoters such as Mg, Si, Ca, Zr and Cr. This catalytic type had initially invented by Imperial Chemical Industries (ICI) in the 1960s, but over the last five decades, it has constantly improved and it is still applied in the methanol synthesis reactors today with the advantages and restriction of this catalyst system. This type of catalyst operated at a pressure interval of 5-10 MPa and a temperature interval of 200-300 degrees Celsius [4].

The methanol production process from syngas is shown by the following reactions: The Eq. (1) is CO hydrogenation reaction (A), Eq. (2) is CO_2 hydrogenation reaction (B), Eq. (3) is the water gas shift reaction (WGS) and Eq. (4) of methanol

dehydration side reaction is considered (DME). The by-product dimethyl ether in Eq. (4) is an undesirable chemical in manufacturing because it is difficult to be removed by the distillation process in the next step. Consequently, the performance of the process will be affected as well as the quality of commercial methanol products will be reduced [2, 4, 6, 7].

$$CO + 2H_2 \rightleftarrows CH_3OH \quad (1)$$

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \quad (2)$$

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

$$2CH_3OH \rightleftarrows CH_3OCH_3 + H_2O \quad (4)$$

The kinetic equations for the above reactions are shown as follows [2, 7-9]:

$$r_{CO} = \frac{k_A K_{CO}[f_{CO} f_{H_2}^{1.5} - f_{CH_3OH} / (K_{P,A} f_{H_2}^{0.5})]}{(1 + K_{CO} f_{CO})(1 + K_{H_2}^{0.5} f_{H_2}^{0.5} + K_{H_2O} f_{H_2O})} \quad (5)$$

$$r_{CO_2} = \frac{k_C K_{CO_2}[f_{CO_2} f_{H_2}^{1.5} - f_{H_2O} f_{CH_3OH} / (K_{P,C} f_{H_2}^{0.5})]}{(1 + K_{CO_2} f_{CO_2})(1 + K_{H_2}^{0.5} f_{H_2}^{0.5} + K_{H_2O} f_{H_2O})} \quad (6)$$

$$r_{WGS} = -\frac{k_B K_{CO_2}[f_{CO_2} f_{H_2} - f_{CO} f_{H_2O} / K_{P,B}]}{(1 + K_{CO_2} f_{CO_2})(1 + K_{H_2}^{0.5} f_{H_2}^{0.5} + K_{H_2O} f_{H_2O})} \quad (7)$$

$$r_{DME} = \frac{k_{DME} K_{CH_3OH}^2 [C_{CH_3OH}^2 - ((C_{H_2O} C_{DME}) / K_{P,DME})]}{(1 + 2\sqrt{K_{CH_3OH} C_{CH_3OH}} + K_{H_2O,DME} C_{H_2O})^4} \quad (8)$$

where C_i is the concentration of the substance i [mol/cm^3], K_i is species adsorption equilibrium constants of substance i, $K_{P,j}$ is equilibrium constants of the reaction j, k_j is the forward reaction rate constant (j = A, B, C, DME) [gmol/g$_{cat}$/s], r is reaction rate [mol/kg$_{cat}$/s], f_i is fugacity of component i [Pa].

The Peng-Robinson-Stryjek-Vera equation of state (PRSV) is used to determine the thermodynamic properties in this study. The PRSV equation has given reliable results for gas phases and polar compounds at a high-pressure system greater than 1 MPa in earlier studies [6]. The perform of simulation by UniSim Design R470 software are given below:

For all cases in this study, the process was fed with 1000 kg/h of syngas, corresponding to 8.760 tons per year of syngas. The syngas feed (composition mole fraction is CO:CO$_2$:H$_2$: 0,16:0,09:0,75) mixed with the circulating gas by the mixer and compressed to a pressure of 40 bar by the compressor. Following that, the compressed

air stream exchanged for heat with the product getting out of the reactor by a heat exchanger before into the reactor. The reactor is a near-isothermal type and it is similar to a shell-tube type heat exchanger with a catalyst placed in the tube, the flow of syngas passed through the catalyst layers and the transformation occurred. The reaction happened in the temperature range 200^{o}C, the heat load is hot water used to circulate outside the reaction tube to heat exchanger. Next, the product flow from the reactor after the process of heat exchange with the feed-in cooled to 40^{o}C before being put into the separator.

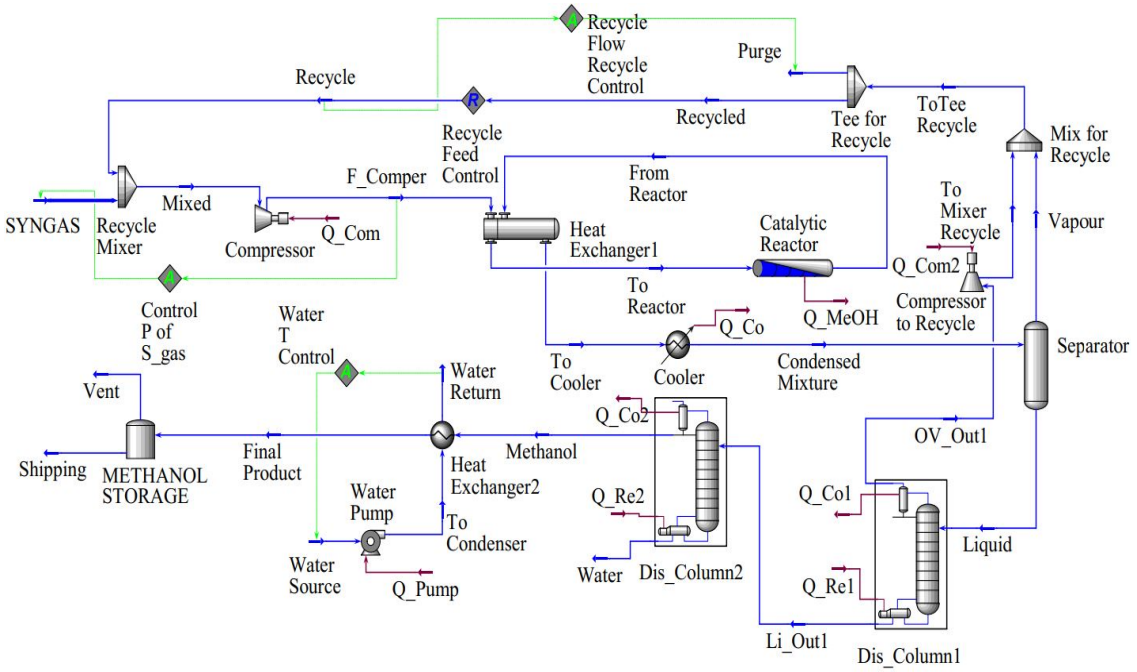

Fig. 2. UniSim Design Process flow diagram of methanol production.

The airflow obtained at the top of the separator tower is recirculated to mix with the original syngas stream and liquid flow from the bottom of the separator tower put into the distillation tower system to separate by-products and refine methanol products. In the first distillation tower, the light gas and dimethyl ether by-products distilled from the methanol product flow which will be recirculated and the bottom flow of the first distillation tower continued to transfer to the second distillation tower to separate most of the water contained in methanol. The product flow in the top of the second distillation column is the pure methanol stream which stored and preserved before being used. The bottom product of the second distillation tower, which is wastewater sent to the plant's general wastewater treatment unit.

3. Results and discussion

After simulation performed, the authors have detected that the purity of methanol product and the production process rate depends on different parameters of this process. So, if these parameters were controlled well, optimum conditions on the methanol production process could be obtained. Based on simulation results, the authors have made observations on the effect of different process parameters of this methanol production. Those study results are shown below:

3.1. The effects of reactor feed temperature on methanol production rate

The data provided in Fig. 3 show that if the reactor feed temperature increases or decreases, both lead to methanol production rate decreases follow. In this case, the best temperature is range 180-200°C, at which the methanol production rate is the most optimal.

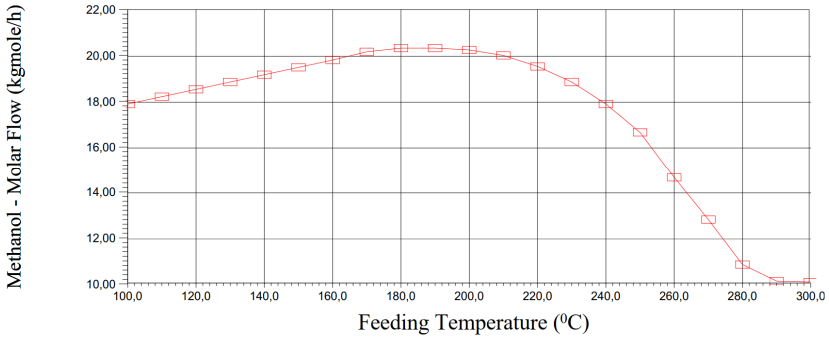

Fig. 3. Effects of reactor feed temperature on methanol production rate.

3.2. The effects of reactor feed pressure on methanol production rate

From Fig. 4, it could be seen that if the reactor feed pressure increases, the methanol production rate goes up to follow. However, from 4 MPa the methanol production rate isn't longer rising markedly. Besides, the increased reactor feed pressure will make operating the system more dangerous and advance production costs. Therefore, the pressure value at 4 MPa could be chosen to become the optimum point in this case.

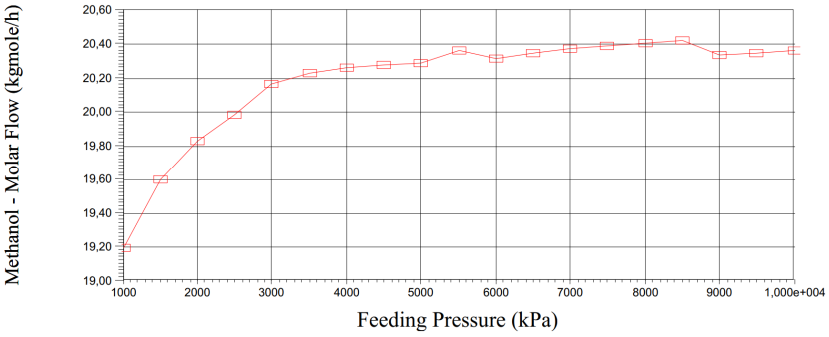

Fig. 4. Effects of reactor feed pressure on methanol production rate.

3.3. The effects of reactor feed temperature on methanol purity

As shown in Fig. 5, the methanol purity decreases with a temperature increase, but known that the methanol production rate will be lower at low temperatures. Therefore, when considering these contradicting aspects then the temperature was chosen for this reaction about 200°C.

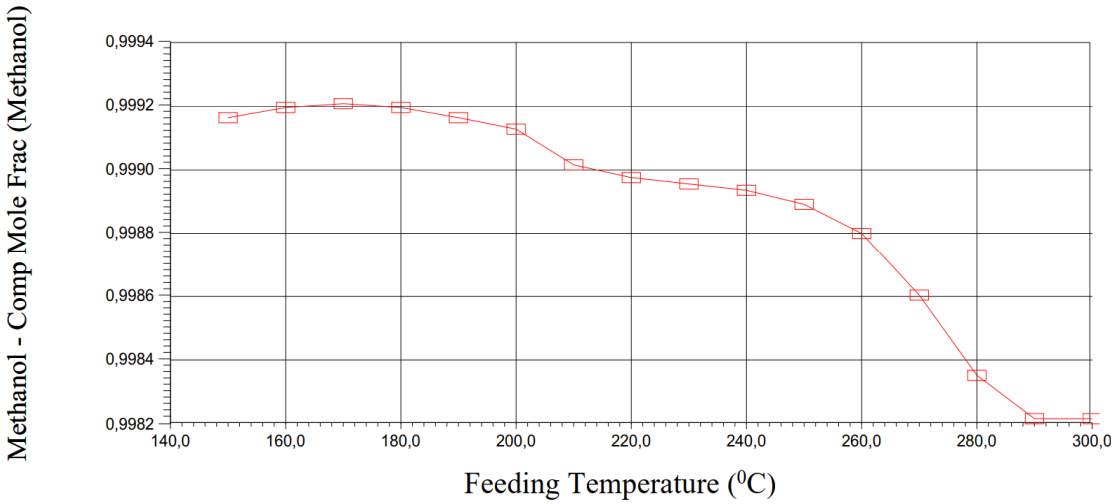

Fig. 5. Effects of reactor feed temperature on methanol purity.

3.4. The effects of reactor feed pressure on methanol purity

As shown in Fig. 6, the methanol purity increases with a tendency to increase feed pressure into the reactor. However, for the decrease in working cost and safety extra of the production line so the feed pressure into the reactor is carried out about 4 MPa.

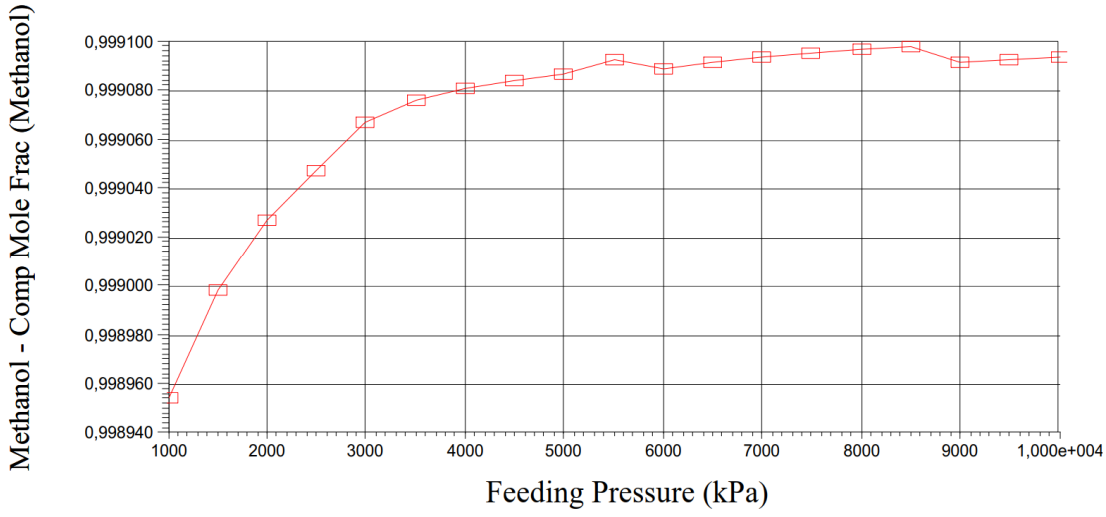

Fig. 6. Effects of reactor feed pressure on methanol purity.

3.5. Syngas feed composition affects the methanol purity and production rate

According to the paper [3], the syngas feed composition characterized by the stoichiometric number S, which is calculated by the formula following [2, 3]:

$$S = \frac{moles\ H_2 - moles\ CO_2}{moles\ CO_2 + moles\ CO} \quad (9)$$

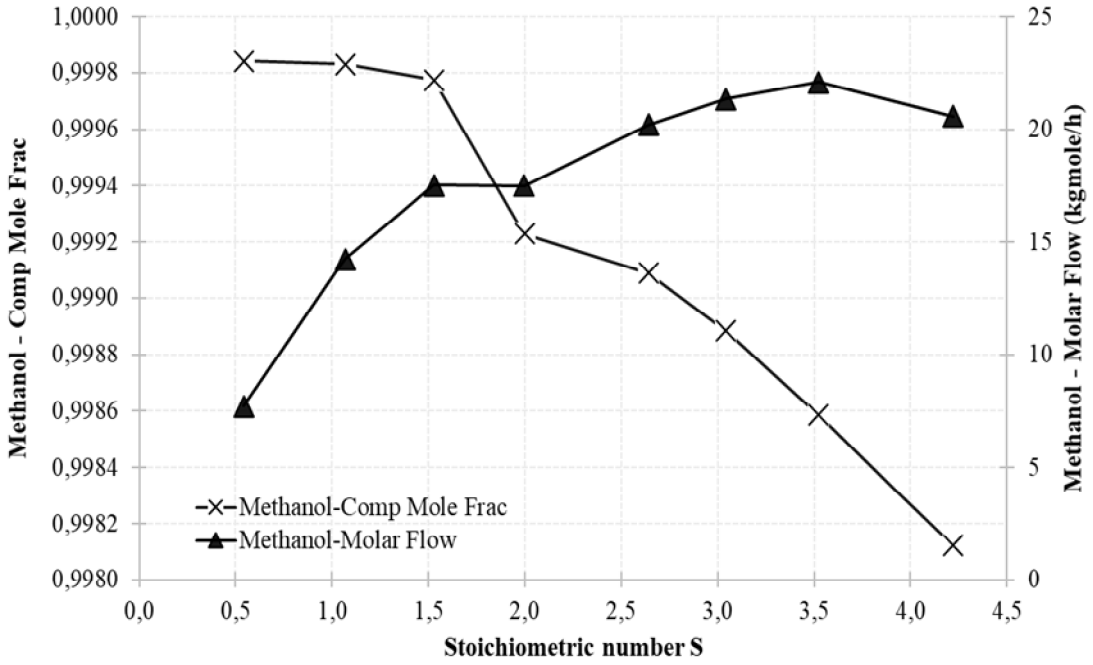

Fig. 7. Effects of syngas feed composition on methanol purity and production rate.

As shown in Fig. 7, it could be seen that if the stoichiometric number S increases, the methanol purity goes down quickly. However, the methanol production rate doesn't rise markedly. This study could be able to see that the best range of the stoichiometric number S is the value from 2 to 3. This result also corresponds to the previous papers' result. The value of more than 2 shows that excess the amount of H_2 while the value less than 2 does that mean lack of H_2 gas [3].

The value stoichiometric number S equals 2,6 (corresponding with syngas feed composition mole fraction is $CO:CO_2:H_2$: 0,16:0,09:0,75) was chosen in this simulation calculation.

3.6. The ratio of recycle stream affects the methanol purity and production rate

As shown in Fig. 8, the methanol purity decreases, when the recycle stream ratio goes up. This case could be explained that is due excess amount H_2 and CO_2 in recycling feed has changed the composition of the original syngas stream and the result

is the water gas shift reaction (WGS) which will shift in the direction of increasing the amount of water according to Le Chatelier's principle. This generated water amount has been pointed out that it makes to decrease the reaction kinetics [2]. It also makes the distillation processes behind load more.

On the other hand, when increased amount of CO_2 also makes the catalyst is deactivated faster due to sintering processes increased. Although the methanol production rate rises markedly, but to ensure the required purity of the methanol product and production rate, the recycle stream ratio is limited to be 0,8.

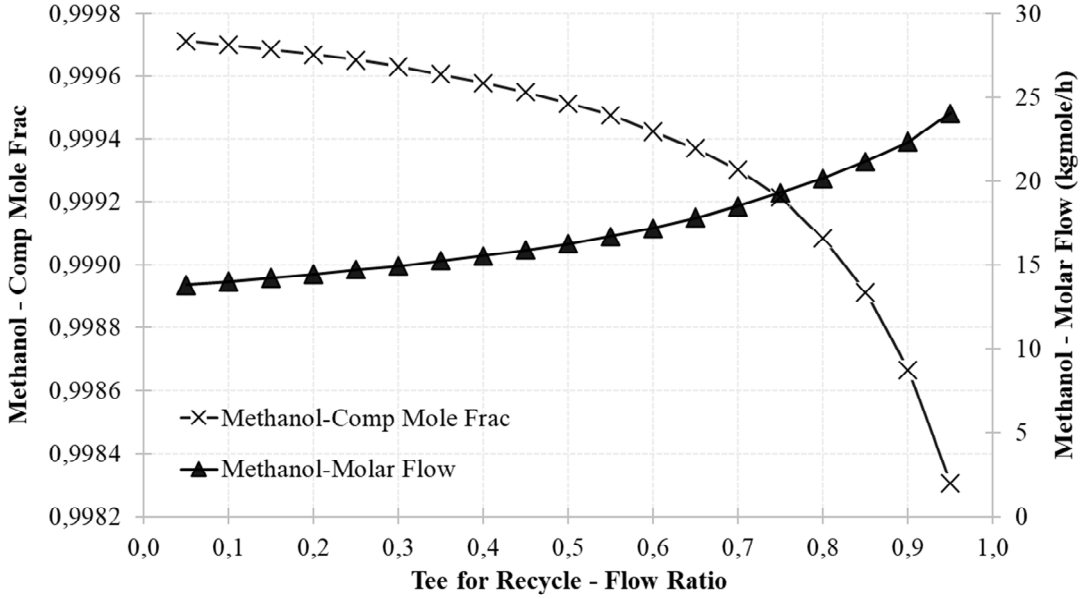

Fig. 8. Effects of recycle stream ratio on methanol purity and production rate.

4. Conclusions

Methanol synthesis is a significant production process in the chemical industry. In this paper, the methanol production line has simulated using UniSim Design R470 software with input data selected based on reference materials. The model of catalyst reactor using the $Cu/ZnO/Al_2O_3$ catalytic type was simulated based on the kinematic data referenced in the documents [1-9]. The simulation results provide an insight knowledge to predict different situations that can happen in the real manufacturing process. By systematically investigating the change of various parameters in the simulation environment, we could predict that the operating reactor feed pressure in the range of 4-5 MPa, reaction feed temperature varying from 180-200°C and the line capacity reached 5.686 tons per year with a purity level of the product can be up to 99,91% when recycling ratio at 0,8. In short, the simulation diagram designed in this

study can be effectively applied to find the optimal operating conditions in the industrial methanol synthesis process.

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NGHIÊN CỨU MÔ PHỎNG QUÁ TRÌNH SẢN XUẤT METANOL TỪ NGUỒN NGUYÊN LIỆU KHÍ TỔNG HỢP BẰNG PHẦN MỀM MÔ PHỎNG UNISIM DESIGN

Tóm tắt: *Trong nghiên cứu này, mô phỏng quá trình tổng hợp metanol từ khí tổng hợp sử dụng phần mềm UniSim Design R470 được thực hiện để phân tích ảnh hưởng của các thông số vận hành đến độ tinh khiết của sản phẩm. Dây chuyền sản xuất bao gồm hai bộ phận chính là phản ứng tổng hợp metanol và tách sản phẩm phụ. Mô hình động học của phản ứng xúc tác dị thể $Cu/ZnO/Al_2O_3$ được tham khảo trong các công trình đã công bố để mô phỏng cho thiết bị phản ứng dòng đẩy. Các số liệu kết quả thu được từ mô phỏng cho thấy rằng năng suất và độ tinh khiết của sản phẩm bị ảnh hưởng bởi ba yếu tố chính là tỉ lệ dòng hồi lưu, nhiệt độ và áp suất phản ứng. Dựa trên phân tích các thông số, điều kiện hoạt động hiệu quả được tìm thấy tại tỉ lệ dòng hồi lưu 0,8 và nhiệt độ, áp suất phản ứng tương ứng được duy trì trong khoảng 180-200^oC và 4-5MPa. Ở điều kiện vận hành này, độ tinh khiết của metanol đạt hơn 99,9% và có thể được sử dụng là nhiên liệu sạch, dung môi.*

Từ khóa: Tổng hợp metanol; mô phỏng; phần mềm UniSim Design; khí tổng hợp.

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