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Research Article

Advancement of Methanol Purity in CO_2 Hydrogenation Process Through Design Optimization, Multistage Compression Simulation, and Purification Model Refinement

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Abstract

Rising greenhouse gas emissions, particularly CO_2, present significant environmental challenges. The goal of this study is to improve methanol synthesis using CO_2 hydrogenation, with an emphasis on increasing purity. To accurately restrict temperature rises during CO_2 compression, we did simulations with Aspen HYSYS V11 and a multistage compression approach. Two notable alterations included the insertion of an absorber unit to improve methanol purity and the recycling of separator outputs. The results show that these process innovations save energy and raw resources while significantly improving methanol output. The findings demonstrate the viability of CO_2 hydrogenation as an environmentally beneficial method of producing methanol, which reduces greenhouse gas emissions while still providing a viable chemical feedstock.

Keywords: Methanol; CO2 Hydrogenation; Process Optimization; Improvement; Product Purity Enhancement

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1. Introduction

Nowadays, it is widely assessed that greenhouse gas (GHG) emissions are one of the most currently challenging environmental issues and that carbon dioxide is the largest anthropogenic GHG sources. Greenhouse gas (GHG) emissions are one of the most important environmental issues of the twenty first century. The largest source of GHG is the carbon dioxide and its emission has tremendously increased in the last decades, mainly due to fossil fuels combustion for the power generation and the automotive transportation [1]. GHG emissions have dramatically increased since the beginning of the industrial era: in 2018, the average concentration of CO_2 was 407 ppm, which is about 40% higher than in the mid-1800s, with an average growth of 2 ppm/year in the last ten years and even 3 ppm/year since 2015. Among the human activities producing GHG, the combustion of fuels for electricity and heat is the largest source of CO_2 emissions representing more than 42% of the estimated anthropogenic CO_2 emissions, where 43% and 26% of these emissions are respectively dedicated to industrial and residential needs. Apart from the energy generation, direct CO_2 emissions from the automotive transportation (23%) and industrial processes (19%) are also main contributors of the anthropogenic CO_2 emissions [2]. Furthermore, the global energy demand is expecting to increase throughout the years and even double by 2050 [3]. Fossil fuels utilization will thus remain predominant in the energy sector in comparison to the use of renewable energy even if its penetration in the market is also increasing through time.

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In previous research, the simulation conducted has added a recycle system from the top product of the separator which has the potential to increase the purity of the final result of methanol production. However, the recycle system from previous research did not add any unit in the system that support operating conditions. Unsuitable operating conditions will cause the reaction not to run optimally [4], so in the modification, supporting unit such as tee and compressors were added to the recycle system. The tee unit is used to separate the outflow from the separator which predominantly contains CO_2 and the rest is methanol and water. The compressor unit is added to regulate the pressure to suit operating conditions and the recycle process can run optimally. The CO_2 hydrogenation process in the production of methanol requires operating conditions at high temperatures and pressures. In its modification, multi-stage compression is carried out. When the gas is compressed, its temperature increases. In multistage compression, the gas can be cooled between compression stages, which is called intercooling. This inter-stage cooling process helps reduce the temperature of the gas before entering the next compression stage, thereby increasing the overall thermal efficiency of the process. This also reduces the risk of thermal damage to the compressor equipment [5].

In previous research, the output from the separator was directly forwarded to the distillation column unit. The bottom product separator still contains carbon dioxide compounds that should be separated first to increase the purity of methanol. Therefore, in this modification, there is an additional absorber unit used to separate the unreacted CO_2 components so that high-purity methanol can be produced [6]. Methanol is generally used as a solvent and/or as a raw material for the production of different chemicals such as: formaldehyde, acetic acid, methyl methacrylate, dimethyl terephthalate, methylamines, dimethyl ether, methyl-tert-butylether and chloromethanes [7]. Also, light olefins (ethylene and propylene) can be obtained with a methanol-to-olefin process [8,9]. In addition, methanol can be used as an alternative fuel in the transportation sector [10,11] and in fuel cell applications [12]. Therefore, to be able to increase the purity of methanol so that it can be utilized optimally, process modifications are carried out such as adding units to the recycle and multi-stage compression so that the operating conditions are running properly to minimize damage to the equipment. The addition of an absorber unit for purification is also very useful for the process of separating the remaining CO_2 components. Thus, through this modification, methanol and water will be separated and produce high-purity methanol.

2. Methods

2.1 CO_2 Hydrogenation

Hydrogenation of CO_2 to methanol is a chemical process that converts carbon dioxide gas (CO_2) to methanol (CH_3OH) using hydrogen (H_2) as a reagent. The production of methanol from CO_2 is a profitable step both economically and environmentally. It contributes to solving the problem of climate change by reducing greenhouse gas emissions [8]. Thermodynamically, CO_2 is a quite stable molecule, owing to its high oxidation state and standard Gibbs free energy (-394.38 kJ.mol^{-1}). The introduction of other reactants with higher Gibbs free energy (such as H_2) can promote CO_2 conversion smoothly. Hydrogenation of CO_2 to methanol reaction is an exothermic and volume-reduction process, leading to it being more favorable for reactions in a lower temperature and higher pressure [13]. CO_2 can also be converted to CO products via the RWGS reaction, which is endothermic. In that case, the reactor model must be designed efficiently. The reactor must be able to remove the heat released from the methanol synthesis reaction to keep the reactor in isothermal conditions. Furthermore, water is produced as a by-product of methanol synthesis from CO_2 [14]. The reaction pathway for methanol synthesis from hydrogen and carbon dioxide involves two steps [15]:

The first reaction: reverse water-gas shift reaction:

$$CO_2 + H_2O \rightleftharpoons CO + H_2O \quad \Delta H°_{298.15\,K} = 41.2 \text{ kJ.mol}^{-1} \quad (1)$$

Secondary reaction, CO_2 hydrogenation:

$$CO + 2H_2 \rightleftharpoons CH_3OH \quad \Delta H°_{298.15\,K} = -90.4 \text{ kJ.mol}^{-1} \quad (2)$$

2.2 Methods to Increase Purity of Methanol

Simulations were carried out using Aspen HYSYS V11 by adding components such as Hydrogen, Carbon dioxide, Methanol, and Water. The fluid package used is Prandtl-Twu. CO_2 gas causes a significant increase in temperature if compression is performed in a single stage. A multi-stage compression process is added to avoid overheating by providing an inter-stage cooling system. The intercooler serves to cool the CO2 gas after each compression stage, reducing the gas temperature and allowing compression to be performed more efficiently [16]. The top product removed from the V-100 separator unit is recycled. This recycle is done with the addition of one tee unit and one compressor unit. The tee is

added to direct the flow back to the initial processing. While the compressor is added to adjust the pressure in the recycle to the pressure in the early processing. The top product from the V-100 separator contains a dominant CO_2 component, with a small amount of methanol remaining. This CO_2 is recycled for efficient material reutilization and also as a preventive measure to reduce atmospheric carbon emissions. The V-101 separator produces carbon dioxide, methanol, and water. The bottom product is forwarded to the T-101 absorber unit to remove the unwanted CO_2 component [17]. The top product contains carbon dioxide, while the bottom product contains methanol and water. The bottom product is further separated in the T-100 distillation column unit to produce high purity methanol components. The high purity methanol can be seen as the distillate product in the T-100 distillation column while the water will separate from the methanol and become the residue product. This happens because the boiling point of methanol is lower than water [22,23].

3. Results and Discussion

3.1 Basic Process Flow Diagram of Methanol Production

Basic process flow diagram of methanol production is depicted in Figure 1, while the Aspen HYSYS simulation of the basic (unmodified) process is presented in Figure 2. Different kinetic models were proposed to describe the methanol production from CO_2 and H_2 [18]. The kinetic models by Van den Bussche and Froment [19] and Graaf *et al.* [20] are most frequently used. The VdB-F (Van den Bussche and Froment) reaction mechanism assumes that CO_2 hydrogenation produces methanol, as well as CO, the latter by means of the Reverse Water Gas Shift (RWGS) that takes place simultaneously to methanol synthesis. When the reactor feed contains CO_2, H_2 and CO (syngas), steam produced by reaction 1 may react with CO to obtain CO_2, made available for hydrogenation to methanol. On the other hand, the Graaf reaction mechanism assumes that CO and CO_2 hydrogenation are both involved in methanol synthesis; besides these two reactions, WGS also takes place. The methanol reaction is exothermic with a reduction in the mole number, as shown by the stoichiometric expression in Equation (3) while the reverse water gas shift (RWGS) is an endothermic reaction without change in the mole number, i.e. relatively high pressure levels are utilized to obtain higher conversions [18,21].

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H°_{298.15\ K} = -49.2\ kJ.mol^{-1} \qquad (3)$$

For the determination of the nature of the reaction (exothermic/ endothermic) and the direction of the reaction (reversible/irreversible), it is necessary to calculate the standard heat of reaction ($\Delta H°_{298.15\ K}$) at 1 bar and 298.15 K based on standard heat of formation of the reactants and products. The value of $\Delta Hf°$ and $\Delta Gf°$ can be seen in Table 1.

Standard heat of reaction at 298.15 K ($\Delta H°_{298.15\ K}$):

$$\Delta H°_{298.15\ K} = \sum \Delta H_f° \text{ product} - \sum \Delta H_f° \text{ reactant}$$

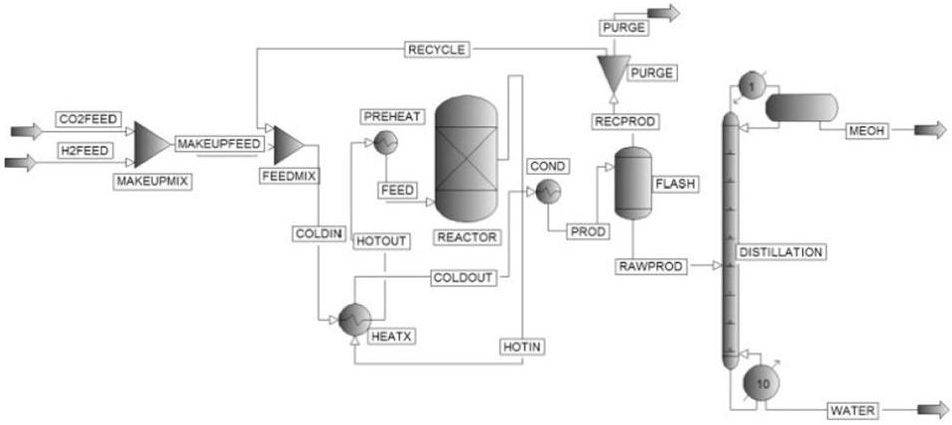

Figure 1. Basic process flow diagram (unmodified) of synthesis methanol [23]

Table 1. The value of $\Delta Hf°$ and $\Delta Gf°$ of compounds

Compounds	Molecular Formula	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)
Carbon dioxide	CO_2	-393.510	-394.370
Hydrogen	H_2	0	0
Methanol	CH_3OH	-200.940	-162.320
Water	H_2O	-241.814	-228.590

$= (\Delta H_f° CH_3OH + (\Delta H_f° H_2O))$
$- (\Delta H_f° CO_2 + (\Delta H_f° H_2))$
$= (-200.940 + (-241.814)) = - (-393.510 - 0) = -49.2$ kJ/mol

Based on the calculations, we get the value $\Delta H°_{298.15\ K}$ = -49.2 kJ/mol, which is a negative value so that the reaction is exothermic, Gibbs Energy ($\Delta G°_{298.15\ K}$):

$\Delta G°_{298.15\ K}$
$= \sum \Delta G_f°$ product $- \sum \Delta G_f°$ reactant
$= (\Delta G_f° CH_3OH + (\Delta G_f° H_2O))$
$- (\Delta G_f° CO_2 + (\Delta G_f° H_2))$
$= (-162.320 + (-228.590)) = - (-394.370 + 0) = 3.460$ kJ/mol

At T_1 = 298.15 K, the equilibrium constant (K_0) in the standard state:

$$\Delta G°_{298.15\ K} = -RT \ln K$$
$$\ln K_1 = -\frac{\Delta G°_{298.15\ K}}{RT} = \frac{3.460\ \text{kJ/mol}}{8.314\ \text{kJ/kmol K} \times 298.15\ \text{K}}$$
$$K_1 = 2.48 \times 10^{-1}$$

Equilibrium constant (K_1) at the ractor temperature: T = 373.15 °K

$$\ln \frac{K_2}{K_1} = \frac{-\Delta H_R°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$\Delta H°_{298.15\ K}$ = Standard heat of reaction at 298.15 °K

$$\ln \frac{K_2}{2.48 \times 10^{-1}} = \frac{-49.2\ \text{kJ/mol}}{8.314\ \text{kJ/kmol.K}}\left(\frac{1}{373.15\ \text{K}} - \frac{1}{298.15\ \text{K}}\right)$$
$$\ln \frac{K_2}{2.48 \times 10^{-1}} = 3.98 \times 10^{-3}$$
$$K_2 = K_1 \times 0.0184 = 4.56 \times 10^{-3}$$

The K values of the reactions are relatively small, so the methanol synthesis reaction is reversible.

3.2 Modified Process Flowsheet and Simulation

To optimize methanol efficiency, a process modification was made using a multi-stage compressor for the CO_2 gas feedstock. CO_2 gas causes a significant temperature increase when compressed in a single stage. A multi-stage compression process is added before the feedstock is mixed in the MIX-100 mixer unit to avoid overheating by providing an inter-stage cooling system. The intercooler serves to cool the CO_2 gas after each compression stage, reducing the gas temperature and allowing compression to be performed more efficiently. Process modifications are also made by adding a recycle of the top product of the V-100 separator so that it returns to the MIX-101 mixer. Recycling of the top product can be done by adding one tee unit and one compressor unit. The tee unit is added for flexible flow division because the flow from the top product of the separator is not completely separated. The input from the top product of this separator is mostly carbon dioxide, then methanol, and water. Meanwhile, a compressor unit is added to maintain pressure stability in order to achieve the required reaction conditions in the mixer. Furthermore, the recycle stream carries the dominant carbon dioxide (CO_2) reactant from the mixer to the methanol synthesis reactor. The bottom product of separator V-101, which contains the dominant methanol component, is separated from CO_2 in the absorber unit. The output of the T-101 absorber contains methanol and water components that are still together. To increase the purity of methanol, a distillation column unit is added to separate methanol and water.

This process modification can increase methanol production while minimizing the use of raw materials and energy. A simulation of the modified methanol synthesis is shown in Figure 3. The modification consists of a multi-stage

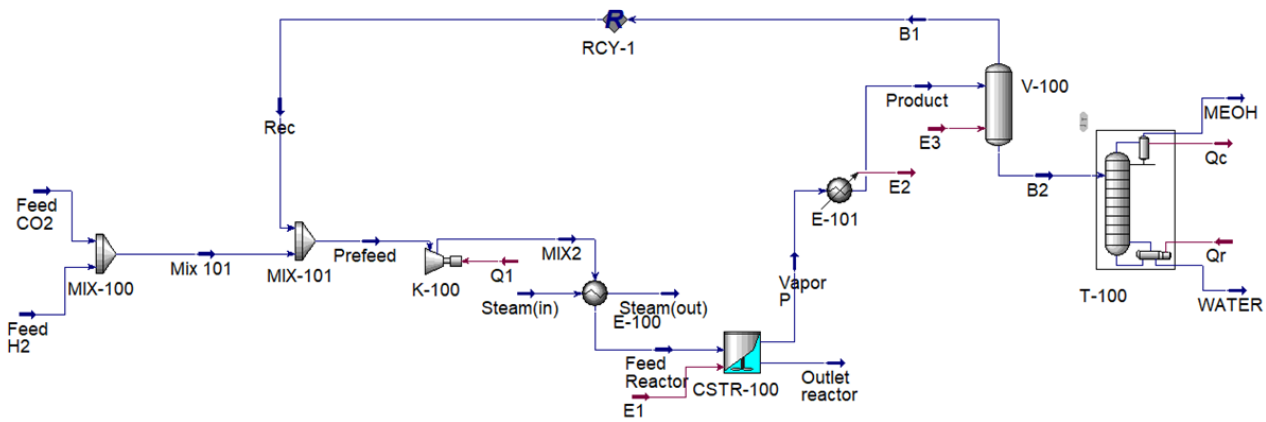

Figure 2. Aspen HYSYS simulation of the basic (unmodified) process

compressor for CO_2 gas, the addition of one tee unit and one compressor unit in the recycle, and an absorber unit before the distillation column unit.

3.3 Process Modification by Increasing Purity of Methanol Product

The modification process flow diagram and Aspen HYSYS V11 simulation are displayed in Figures 3 and 4, respectively. Meanwhile, the mass balance and energy balance results (using Aspen HYSYS simulation) of the methanol production process through the modified CO_2 hydrogenation process are presented in Table S2 (Supporting Information). Purity improvement usually occurs through devices such as separators, absorbers, and distillation columns to achieve high purity. The lower product stream of separator V-100 is first passed into separator V-101 for further separation, while the upper product stream is recycled with the addition of tee TEE-100 and compressor K-101 as an effort to efficiently reuse raw materials so that they are not wasted and also as a preventive measure to reduce atmospheric carbon emissions. The V-101 separator produces a top product with a dominant composition of carbon dioxide, while the bottom product produces a mole fraction composition of 0.0558 CO_2; 0.4717 Methanol; and 0.4725 H_2O. The bottom product from the V-101 separator is forwarded to the T-101 absorber unit to separate the carbon dioxide component that is still in the mixture. The T-101 absorber separates the CO_2 compound from the mixture by producing a mole

Table 2. Methanol purity before and after modification ratio

Treatment	Methanol Purity (%)	
	Top Product	Bottom Product
Before Modification	47.83	0.20
After Modification	95.99	1.42

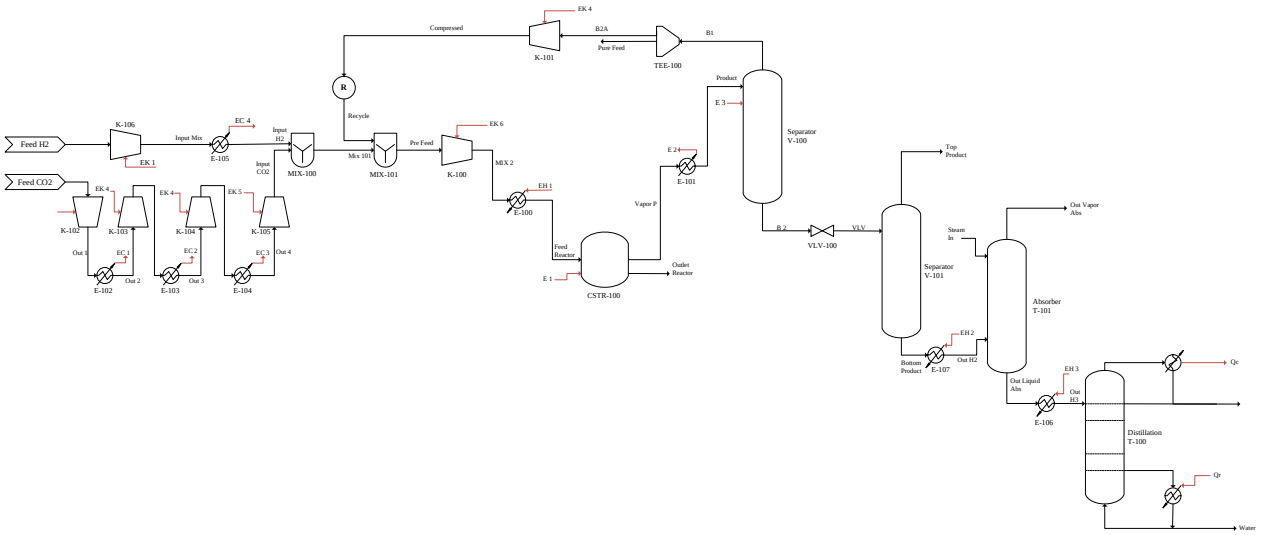

Figure 3. Process flow diagram (modified) of synthesis methanol.

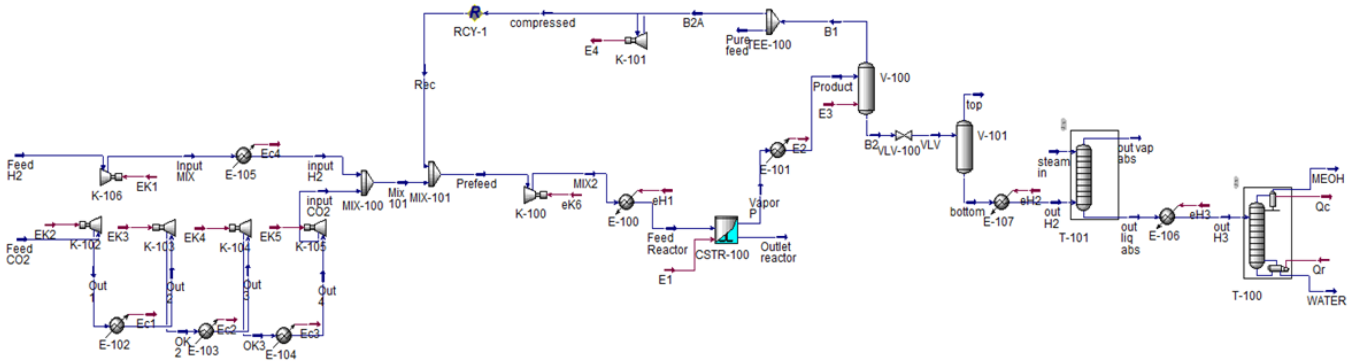

Figure 4. Aspen HYSYS simulation of modified process for synthesis methanol

fraction composition of 0.9507 CO_2 and 0.0493 H_2O. The bottom product of absorption results in a mole fraction composition of 0.3197 Methanol; 0.6706 H_2O; and a little CO_2 of 0.0097. To separate methanol from water to improve the purity of the methanol composition, a distillation column unit must be added. The bottom product of T-101 absorption is used as input for purification in the distillation column. The distillation process in the T-100 column produces methanol as a distillate product with a mole fraction of 0.9599 methanol (Table 2). Meanwhile, water is released as a residue product with a mole fraction composition of 0.9858. Therefore, this modification process can increase the purity of methanol to 95.99% as distillate product and water released as residue product by 98.58%.

4. Conclusions

Process modifications in methanol production must be made to achieve improved energy and mass efficiency. Through process modification, the plant can optimize feedstock and energy use, reduce environmental impact, and improve operational efficiency. Based on the percentage purity of methanol obtained from the modified simulation, the composition of methanol as the top product is 95.99% and water as the bottom product is 98.58%, indicating that the mixture can be completely separated. This process modification can be applied to the production of methanol with a capacity of 250,000 tons/year. Further research on the methanol synthesis process is required. In particular, an economic analysis is needed to improve the methanol synthesis process to make it more energy efficient and economical in terms of feedstock usage. It is also important to analyze the environmental impact, as the world has started to take environmental issues more seriously in the last decade.

CRedit Author Statement

Author Contributions: S.M. Verani: Conceptualization, Methodology, Investigation, Software, Visualization, Writing, Review & Editing, Supervision; T.L. Azhari: Conceptualization, Methodology, Visualization, Writing, Review & Editing, Project Administration, Validation; N. Ridani: Conceptualization, Methodology, Formal Analysis, Resources, Validation, Writing; M.R. Nurardani: Conceptualization, Methodology, Investigation, Resources, Data Curation, Writing. All authors have read and agreed to the published version of the manuscript.

References

[1] Bellotti, D., Rivarolo, M., Magistri, L., & Massardo, A.F. (2017). Feasibility study of methanol production plant from hydrogen and captured carbon dioxide. *Journal of CO2 utilization*, 21, 132-138. DOI: 10.1016/j.jcou.2017.07.001

[2] Meunier, N., Chauvy, R., Mouhoubi, S., Thomas, D., & De Weireld, G. (2020). Alternative production of methanol from industrial CO2. *Renewable Energy*, 146, 1192-1203. DOI: 10.1016/j.renene.2019.07.010

[3] Varone, A., & Ferrari, M. (2015). Power to liquid and power to gas: An option for the German Energiewende. *Renewable and Sustainable Energy Reviews*, 45, 207-218. DOI: 10.1016/j.rser.2015.01.049

[4] Chin, H.H., Varbanov, P.S., Klemes, J.J., Benjamin, M.F.D., & Tan, R.R. (2020). Asset Maintenance Optimisation Approach in The Chemical and Process Industries - A Review. *Chemical Engineering Research and Design,* 164, 162-194. DOI: 10.1016/j.cherd.2020.09.034

[5] Mendez, H.L., Arenas, T.L., Aldaco, A.T., Gonzales, E.V.T., Cruz, M.S., & Leyte, R.L. (2021). Interstage Pressure of a Multistage Compressor with Intercoolong. *Entropy,* 23, 351. DOI: 10.3390/e23030351

[6] Soo, X.Y.D., Lee, J.J., Wu, W. Y., Tao, L., Wang, C., Zhu, Q., & Bu, J. (2024). Advancements in CO2 capture by absorption and adsorption: A Comprehensive Review. *Journal of CO2 Utilization,* 81. DOI: 10.1016/j.jcou.2024.102727

[7] Van Bennekom, J.G., Venderbosch, R.H., Winkelman, J.G.M., Wilbers, E., Assink, D., Lemmens, K.P.J., & Heeres, H.J. (2013). Methanol synthesis beyond chemical equilibrium. *Chemical Engineering Science*, 87, 204-208. DOI: 10.1016/j.ces.2012.10.013

[8] Dimian, A.C., & Bildea, C.S. (2018). Energy efficient methanol-to-olefins process. *Chemical Engineering Research and Design,* 131, 41–54. DOI: 10.1016/j.cherd.2017.11.009

[9] Montebelli, A., Visconti, C.G., Groppi, G., Tronconi, E., Ferreira, C., & Kohler, S. (2013). Enabling small-scale methanol synthesis reactors through the adoption of highly conductive structured catalysts. *Catalysis Today*, 215, 176-185. DOI: 10.1016/j.cattod.2013.02.020

[10] Abrar, I. Arora, T., & Khandelwal, R. (2023). Bioalcohols as an alternative fuel for transportation: Cradle to grave analysis. *Fuel Processing Technology*. 242. DOI: 10.1016/j.fuproc.2022.107646

[11] Parris, D., Spinthiropoulos, K., Ragazou, K., Giovou, A., & Tsanaktsidis, C. (2024). Methanol a Plugin Marine Fuel for Green House Reduction - A Review. *Energies,* 17(3). DOI: 10.3390/en17030605

[12] Adiyar, S.R., Satriyatama, A., Azjuba, A.N., & Sari, N.K.A.K. (2021). An overview of synthetic polymer-based membrane modified with chitosan for direct methanol fuel cell application. IOP Conference Series: *Materials Science and Engineering,* 1143 (1). DOI: 10.1088/1757899x/1143/1/012002

[13] Fan, W.K., & Tahir, M. (2022). Recent developments in photothermal reactors with understanding on the role of light/heat for CO2 hydrogenation to fuels: A review. *Chemical Engineering Journal*, 427, 131617. DOI: 10.1016/j.cej.2021.131617

[14] Cui, G., Lou, Y., Zhou, M., Li, Y., Jiang, G., & Xu, C. (2024). Review of Mechanism Investigations and Catalyst Developments for CO2 Hydrogenation to Alcohols. *Catalysts*, 14(4), 232. DOI: 10.3390/catal14040232

[15] Phey, M.L.P., Abdullah, T.A.T., Ali, U.F.M., Mohamud, M.Y., Ikram, M., & Nabgan, W. (2023). Reverse water gas shift reaction over a Cu/ZnO catalyst supported on regenerated spent bleaching earth (RSBE) in a slurry reactor: the effect of the Cu/Zn ratio on the catalytic activity. *RSC Advances*, 13(5), 3039-3055. DOI: 10.1039/d2ra07617a

[16] Zhang, C., Wang, X., Shi, X., Bi, J., Huang, X., & You, S. (2024). Performance simulation study of multi-stage compression-throttle water working medium high-temperature heat pump system. *Applied Thermal Engineering*, 247, 123030. DOI: 10.1016/j.applthermaleng.2024.123030

[17] Procopio, M.N., Urquiza, G., & Castro, L. (2023). Analysis of Absorber Packed Height for Power Plants with Post-Combustion CO2 Capture. *Sustainability*, 15 (12), DOI: 10.3390/su15129536

[18] Meyer, J.J., Tan, P., Apfelbacher, A., Daschner, R., & Hornung, A. (2016). Modeling of a methanol synthesis reactor for storage of renewable energy and conversion of CO2. Chemical Engineering Technology, 39 (2), 233-245. DOI: 10.1002/ceat.201500084

[19] Bussche, K.V., & Froment, G.F. (1996). A steady-state kinetic model for methanol synthesis and the water gas shift reaction on a commercial Cu/ZnO/Al2O3Catalyst. *Journal of Catalysis*, 161 (1), 1-10. DOI: 10.1006/jcat.1996.0156

[20] Graaf, G.H., Stamhuis, E.J., & Beenackers, A.A. C.M. (1988). Kinetics of low-pressure methanol synthesis. *Chemical Engineering Science*, 43 (12), 3185-3195. DOI: 10.1016/0009-2509(88)85127-3

[21] Manenti, F., Leon-Garzon, A.R., Ravaghi-Ardebili, Z., & Pirola, C. (2014). Systematic staging design applied to the fixed-bed reactor series for methanol and one-step methanol/dimethyl ether synthesis. *Applied Thermal Engineering*, 70(2), 1228-1237. DOI: 10.1016/j.applthermaleng.2014.04.011

[22] Martinka, J., Rantuch, P., & Wachter, I. (2019). Impact of water content on energy potential and combustion characteristics of methanol and ethanol fuels. *Energies,* 12(18). DOI: 10.3390/en12183491

[23] Aboelela, D. (2024). Converting CO2 into Clean Fuels: A Sustainable Approach. *International Journal of Industry and Sustainable Development*, 5 (2), 29-46. DOI: 10.21608/ijisd.2024.296846.1050