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Research Article

Maximizing Ethylene Production Yield by Modifying the Methanol to Olefin Process with the Addition of a Distillation Tower

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Abstract

Ethylene is a feedstock that produces polyethene and other industrial chemicals such as ethylene oxide. The methanol-to-olefins process is a technology designed to transform methanol into light olefins like ethylene and propylene, which are crucial raw materials in the petrochemical industry. The first reaction involves the production of dimethyl ether and water from methanol. The second reaction consists of the conversion of dimethyl ether to ethylene and water. This paper will explain how to maximize ethylene production yield by modifying the methanol to olefin process. The process modification was carried out by adding a distillation tower. Based on process modifications increased the ethylene quantity from 21,070 tons/year to 179,400 tons/year. The case study results indicate an increasing yield of the product exiting.

Keywords: Ethylene; Methanol to Olefins; Distillation; maximizing yield; Cumene Oxidation

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1. Introduction

Light olefins, such as ethylene, are essential raw materials and foundational molecules within the chemical industry. The global olefin market is expected to expand at a 4.5% annual growth rate starting in 2020, with its value projected to reach USD 329.30 billion by 2028. The rising demand for light olefins is primarily fueled by the growing application of polymers, plastics, and fibers in electronic devices [1]. Alternatively, light olefins are produced mainly through the thermal cracking of naphtha derived from the distillation of crude oil. Another alternative route of olefin production is from natural gas, an alternative approach for producing olefins involves utilizing natural gas to produce methanol, which appears to be a feasible pathway for olefin production, offering the possibility of high yields [2]. Olefins are important raw materials for organic synthesis. Currently, olefins are produced almost exclusively from fossil fuels and oil. Modern technologies, such as methanol-to-olefins (MTO) and methanol-to-propylene (MTP), are available using feedstocks such as biogas, biomass, and coal, thus providing a clean power source for the chemical industry. Methanol is also an important raw material for the sustainable chemical industry [3]. Generally, the MTO reactor product consists of lighter hydrocarbon fractions compared to the conventional thermal cracking process. Far enough for the low price of natural gas and coal as raw materials for methanol production is a critical point. The thing that motivates methanol production is the very large natural gas resource. Ethylene can also be produced from ethane [4].

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The Methanol-to-Olefins (MTO) process is a technology designed to transform methanol into light olefins like ethylene and propylene, which are crucial raw materials in the petrochemical industry. Initially introduced by Union Carbide in 1981, MTO has evolved into a major independent technology for olefin production [5]. The basic Methanol-to-Olefins (MTO) process begins with heating methanol to its gas phase before it is fed into the MTO reactor, where it undergoes dehydration and conversion into dimethyl ether (DME) and water. The reaction mixture, containing DME and unconverted methanol, is then further heated and directed into the reactor. The reactor converts DME and methanol into light olefins, including ethylene and propylene, with a very high conversion efficiency [6]. Currently, two MTO process technologies are available namely Mobil's MTO process and UOP/Hydro MTO process. Mobil's MTO process was demonstrated in a 100 BPD fluid bed facility in Germany. Initially designed for gasoline production, the process was later extended to demonstrate the MTO process. The plant was operated at a pressure between 2.2 and 3.5 bar and a temperature of about 500 °C. The catalyst used was a modified ZSM-5 zeolite type catalyst. At steady state conditions the olefin yield was more than 60% [7].

2. Material and Methods

2.1 Basic Chemical Process Description of Methanol to Olefin Production

In the general process using MTO technology. Starting from the reaction and conditioning section, the methanol feed is converted into a mixture of olefins, then cooled and purified. In the first separation section, the output from the reaction and conditioning section is separated into three products, namely light components, heavy components, and a C2–C3 mixture. The C2–C3 mixture then enters the second separation section, which includes C2 separation and C3 separation. The main purpose of the second separation section is to obtain pure ethylene and propylene as products, with both purities set at the polymer target, namely 99.5 mol% [8]. In the reactor, maximizing methanol conversion and olefin selectivity is the primary goal. However, various parameters influence these factors differently. For instance, increasing the reactor temperature enhances reaction rates and conversion, but olefin selectivity depends on the individual reaction rates and their ratios, which may vary. High temperatures also lead to coke formation, which accumulates on the catalyst surface, reducing its activity and altering the selectivity of desired products. Thus, reactor temperature (T) and catalyst coke content (CC) are critical factors affecting product flowrates and compositions [9].

Ethylene, or ethene, is an unsaturated organic compound that belongs to the most straightforward group of alkene hydrocarbons. Although rarely used directly and more often as a feedstock, ethylene is the petrochemical with the highest production rate globally. In the chemical industry, ethylene is mainly used as a base material to make polymers, plastics, fibers and other organic chemicals, most of which are applied to final consumption products, especially in packaging [10]. Methanol is the most crucial building block in the chemical and pharmaceutical industry and in the production of synthetic hydrocarbons. The output of high-demand chemical commodities such as ethylene and propylene (methanol-to-olefins) [11].

MTO is one of the advances that can create fundamental petrochemicals. Methanol is delivered primarily catalytically using syngas, a profitable gas blend of hydrogen and carbon monoxide. Methanol is utilised in huge volumes to offer various product chemicals. Syngas can be obtained from distinctive carbonaceous assets by gasifying regular gas, coal, or biomass. Thus, this preparation presents a reasonable elective to create base chemicals from assets other than rough oil [12].

The transformation of methanol to olefins (MTO) is a complex catalytic process. The reactions involved in this process are developed in two reaction stages. The first reaction is an equilibrium reaction involving the production of dimethyl ether and water from methanol (Equation 1). Then, the second reaction involves the conversion of dimethyl ether to ethylene and water (Equation 2).

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \quad (1)$$

$$CH_3OCH_3 \longrightarrow C_2H_4 + H_2O \quad (2)$$

The thermodynamic analysis allows the reaction network to be realised in the first step, which is hugely significant. The thermodynamic properties of the reactions of methanol to dimethyl ether (Equation (1)) calculated at a standard temperature of 298 °C are given in Table 1 [13].

The following expression gives the equilibrium constant as a function of temperature [9].

$$-R \ln KE = \frac{\Delta G}{T} \quad (3)$$

$$\frac{\Delta G}{T} = -\frac{6836}{T} + 2.32 \ln T - 0.475 \times 10^{-3} T - 0.11 \times 10^{-6} T^2 - 10.92 \quad (4)$$

Simulation of this production process was carried out using the HYSYS Aspen application.

The two reactions mentioned earlier will be included as reaction sets 1 (equilibrium, Equation (1)) and 2 (conversion, Equation (2)). In reaction set 1, the K_{eq} value calculated in the previous calculation is entered. Then, in reaction set 2, a conversion value of 95% is entered. The two reaction sets developed were attached to the selected Fluid Package, which was NRTL, before being used in the Simulation Environment of the Aspen HYSYS [14].

2.2 Strategy of Modification on istillation Unit

A distillation column is a tool that is widely used to separate various chemical substances. The basic theory of this separation is the difference in boiling points of the separated components. At the bottom of the distillation column is a heat source, namely the reboiler. At the top of the distillation column is a condenser that cools the vapor from the top stage into a liquid and a container that holds the liquid, allowing some of this liquid to be returned as reflux and some as distillate [15].

Separation of components from a mixture is generally done by distillation [16]. Distillation is dividing a mixture of substances based on stark variations in boiling point and vapor pressure. The distillation column is one of the complex pieces of process equipment for modeling and controlling important parts of a separation and purification process often used by the chemical industry. The difference in vapor pressure will cause the vapor phase to be in equilibrium with the liquid phase, resulting in significant differences in composition. The vapor phase contains more components with low vapor pressure, while the liquid phase contains more components with high vapor pressure [17]. Yuting *et al.* [18] proposed a distillation system as an alternative design for ethylene separation, which is determined to be more economical than membrane cascade configuration where the economic reduction compared with traditional cryogenic distillation was not investigated.

The use of distillation in this paper is to separate ethylene into products. Before entering the distillation, the reactor's inlet temperature or output temperature is minus, so we add a heater so there is no pressure drop in distillation. Then, after distillation, ethylene is not produced alone, but there is a mixture of dimethyl ether because the boiling point between ethylene and dimethyl ether is similar. After that, we obtained an ethylene purity of 95%. Finally, we will obtain the yield by dividing the ethylene produced and the initial methanol or mathematically found in Equation (5).

$$\%Yield = \frac{Mol\ of\ Produced\ Ethylene}{Mol\ of\ Initial\ Methanol} \times 100\% \quad (5)$$

3. Results and Discussion

3.1 Simulation of Basic Process

Simulation of ethylene production through the Methanol to Olefins (MTO) process was conducted using Aspen HYSYS software. The feed methanol capacity for industrial ethylene production is 2 million tons per year. The simulation of the basic process is shown in Figure 1, while the process flow diagram of the basic process is shown in Figure 2. In the basic process, less equipment is used. The process synthesises ethylene from methanol through two main steps: converting methanol to dimethyl ether in an equilibrium reactor and converting dimethyl ether to ethylene. The simulation utilises the Non-Random Two-Liquid (NRTL) model and achieves a conversion rate of 98.29% [19].

In addition, other basic MTO processes can be seen in the simulation using Aspen Hysys software in Figure 3 and the process flow diagram in Figure 4 with the same two main stages, starting with the conversion of methanol to dimethyl ether and then converting it to ethylene in the conversion reactor. Distillation is also used to separate the dimethyl ether produced from the reactor, thus increasing the plant's efficiency to achieve an ethylene production purity of 95%. The difference between the two basic processes is the reactor used where the first basic process uses an equilibrium reactor, and the second basic process uses a plug flow reactor [13].

Then, the basic processes, one and two, are combined. However, in converting methanol to dimethyl ether and then to ethylene, an equilibrium reactor is considered more suitable because it can provide better results in terms of product purity. Hence, this combination uses an equilibrium reactor. PFR reactors require reaction kinetics information to operate, including activation energy and pre-expression factors. By replacing the PFR with an equilibrium

Table 1. The value of ΔH° and ΔG° of compounds

No.	Reaction	ΔH° (kJ.mol-1)	ΔG° (kJ.mol-1)
Eq.1	$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$	-22.57	-16.19
Eq.2	$CH_3OCH_3 \rightarrow C_2H_4 + H_2O$	-6.42	-48.02

reactor, improved conditions and process design can be achieved to achieve higher efficiency in ethylene production more efficiently. In this combination, an ethylene product of 21,070 tons/year was obtained and by using Equation (5), the yield value of 5.27% is obtained. The Aspen HYSYS software simulation for this process combination can be seen in Figure 5, and the process flow diagram can be seen in Figure 6.

It is important to increase ethylene production yields to meet the growing global market demand, where ethylene plays a crucial role as a key raw material in the chemical industry. Ethylene produces a wide array of commercially important products, such as polyethylene, polymers, and fibers, accounting for about 60% of the total ethylene consumption. Along with increasing demand and breadth of applications, ethylene is expected to remain a major component in the petrochemical industry, making production efficiency crucial [20]. One method to increase ethylene production is through distillation of the bottom product of the separator. By utilizing a distillation column, components are separated based on differences in boiling points [21]. In addition to producing high-quality ethylene, this process also supports recycling unused hydrocarbons, improves process efficiency, and reduces waste, thus meeting industry standards [22].

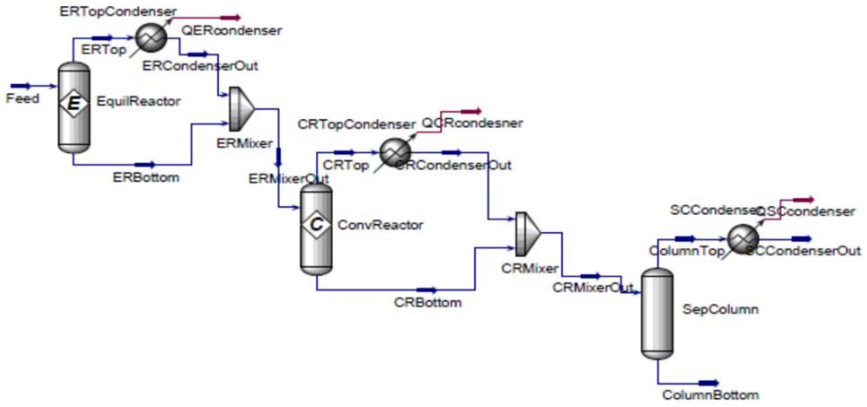

Figure 1. Simulation using Aspen HYSYS for the first basic process

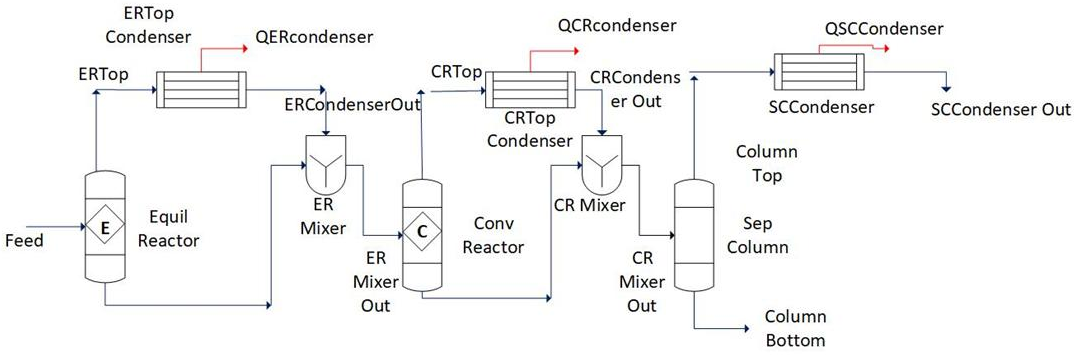

Figure 2. Process flow diagram for the first basic process

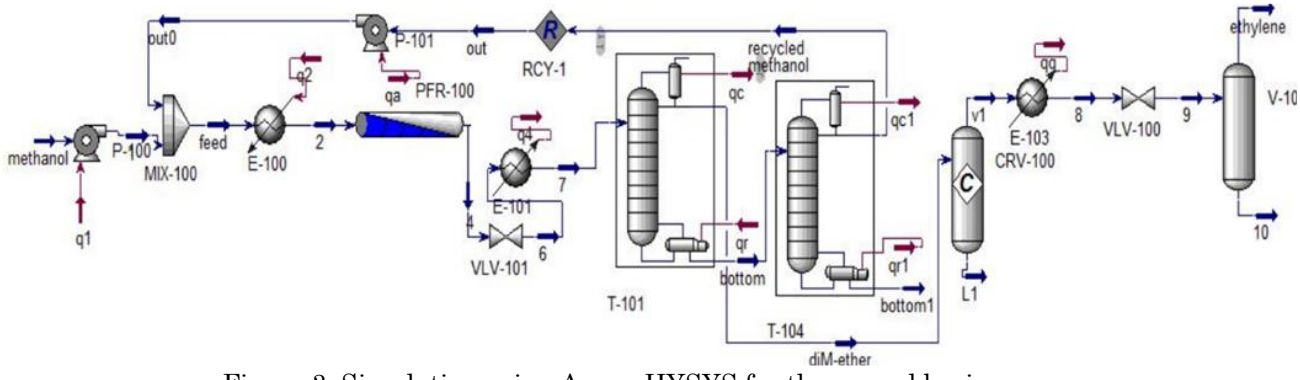

Figure 3. Simulation using Aspen HYSYS for the second basic process

3.2 Simulation of Modified Process

To increase ethylene production and improve the purity of the final product, a distillation tower can be integrated into the process as an essential separation tool. The primary function of the distillation tower is to segregate hydrocarbon mixtures based on differences in their boiling points, enabling more effective separation of ethylene from other hydrocarbon components. In this modified process that have been shown in Figures 7 and 8, an ethylene product of 180,600 tons/year was obtained and by using Equation (5), the yield value of 44.85% was obtained. The comparison of the modified process and unmodified process can be seen in Table 2, while the material and energy balances of this process can be seen in Tables S1 and S2 (Supporting Information).

Modified flow diagram, adding further distillation to produce purer ethylene. As a result, all high boiling fractions, which are most susceptible to resinification, pass through the entire distillation system [23]. For the second distillation unit, the product-rich electrolyte is recycled to a fixed volume concentration of methanol, so that the electrolyte flow rate used for the distillation capital cost can be measured [24]. In the third step, the bottom component of the separator will be reheated and then re-entered

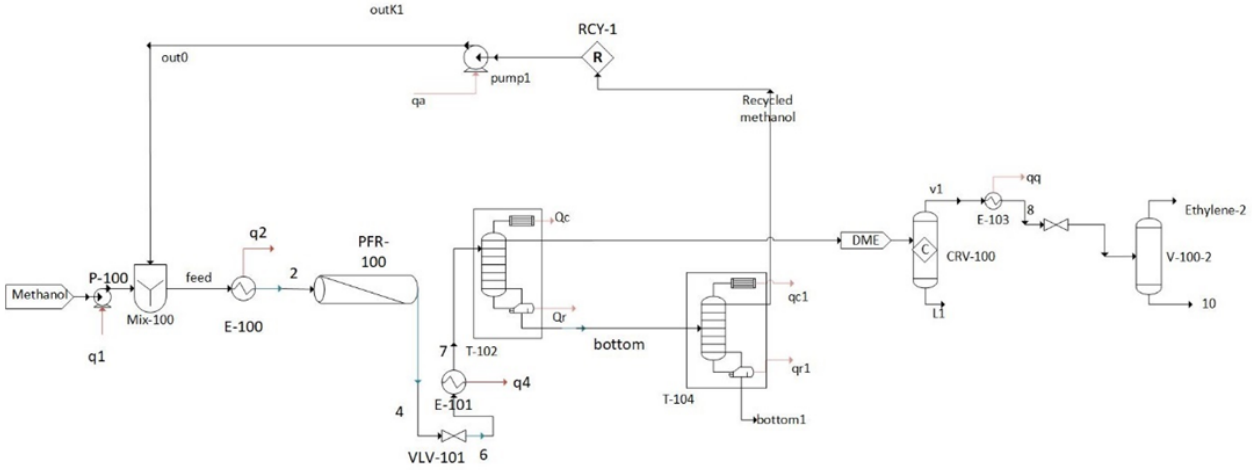

Figure 4. Process flow diagram for the second basic process

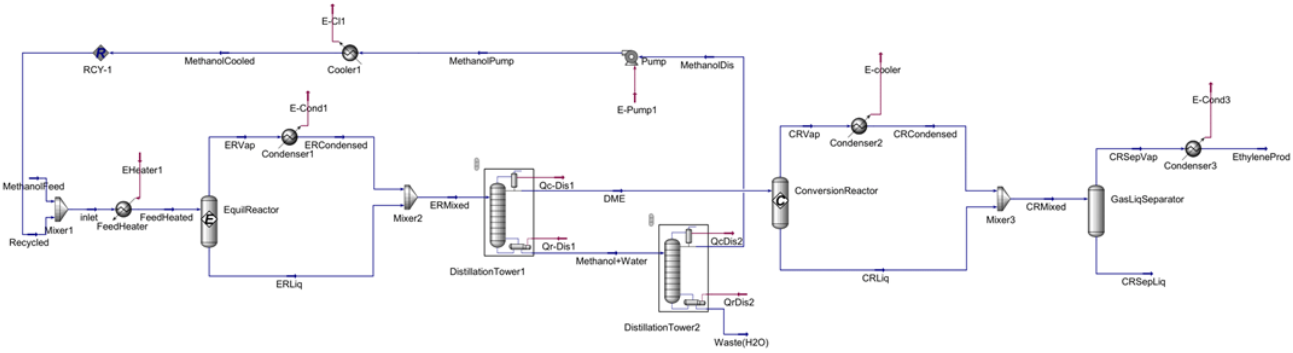

Figure 5. Simulation of unmodified using Aspen HYSYS for ethylene production

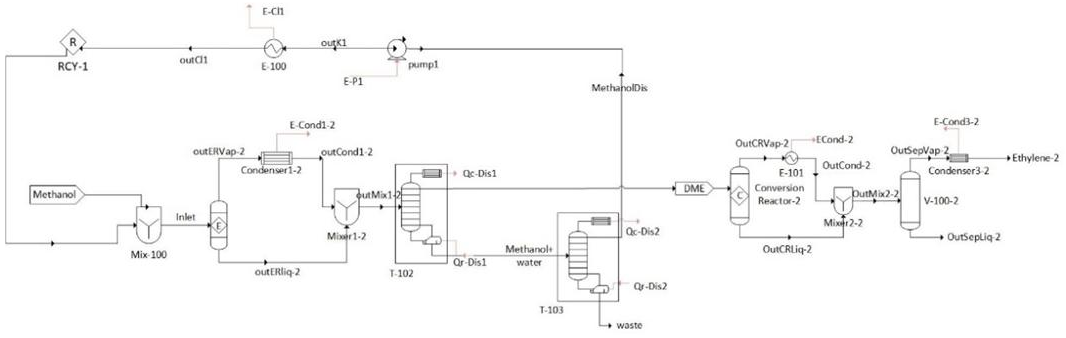

Figure 6. Process flow diagram for process combinations

the distillation unit to produce even purer ethylene products [25].

4. Conclusion

This study successfully optimized the ethylene production process from methanol (MTO) by combining and modifying it by adding a distillation tower at the end of production. With the modification, ethylene production was increased from 21,070 tons/year to 180,600 tons/year. Using Aspen HYSYS simulation, the proposed design achieves high process efficiency while maintaining the 95% ethylene purity target. This finding emphasizes the important role of using a distillation tower when there are compounds in the stream to be removed. Future research can explore determining other types of separation while maintaining energy efficiency to maximize sustainability.

CRediT Author Statement

Author Contributions: A.R.H. Sitio: Software, Conceptualization, Methodology, Investigation, Resources, Data Curation, Review and Editing, Supervision; D.S. Azahra: Conceptualization, Methodology, Formal Analysis, Data Curation, Writting Draft Preparation, Visualization, Software, Project Administration; F.N. Zahrani: Validation, Writing, Review and Editing, Data Curation; R.Z.M. Martantri: Investigation, Software, Resources, Writing, Review and Editing; S.N. Ajitira: Investigation, Resources, Writing, Review and Editing, Validation.All authors have read and agreed to the published version of the manuscript.

References

[1] Chernyak, S.A., Corda, M., Dath, J. P., Ordomsky, V. V., & Khodakov, A. Y. (2022). Light olefin synthesis from a diversity of renewable and fossil feedstocks: state-of the-art and outlook. *Chemical Society Review*, 51(18), 7994-8044. DOI: 10.1039/D1CS01036K

[2] Amghizar, I., Vandewalle, L. A., Van Geem, K. M., & Marin, G. B. (2017). New trends in olefin production. *Engineering*, 3(2), 171-178. DOI: 10.1016/J.ENG.2017.02.006

[3] 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

[4] Hedayati Moghaddam, A. (2022). Simulation and optimization of separation section in methanol to olefin (MTO) process based on statistical approach. *Chemical Papers,* 76(8), 4787-4794. DOI:10.1007/s11696-022-02190-4

Table 2. Ethylene product before and after modification ratio

Treatment	Ethylene product (tons/year)	%Yield
Before Modification	21,070	5.27%
After Modification	180,600	44.85%

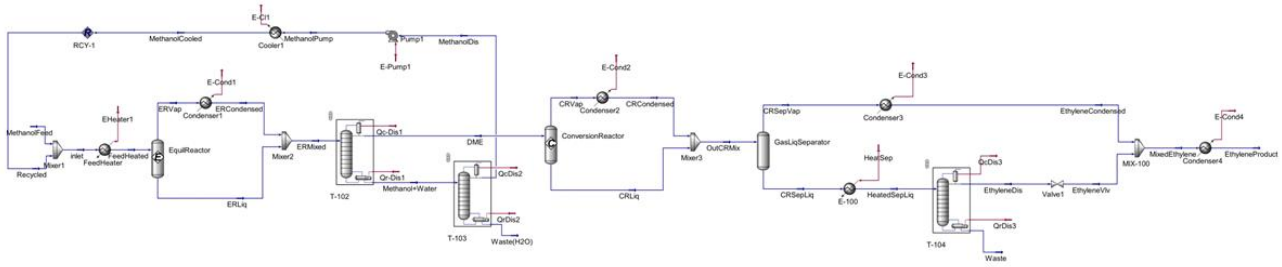

Figure 7. Simulation of modified using Aspen HYSYS for ethylene production

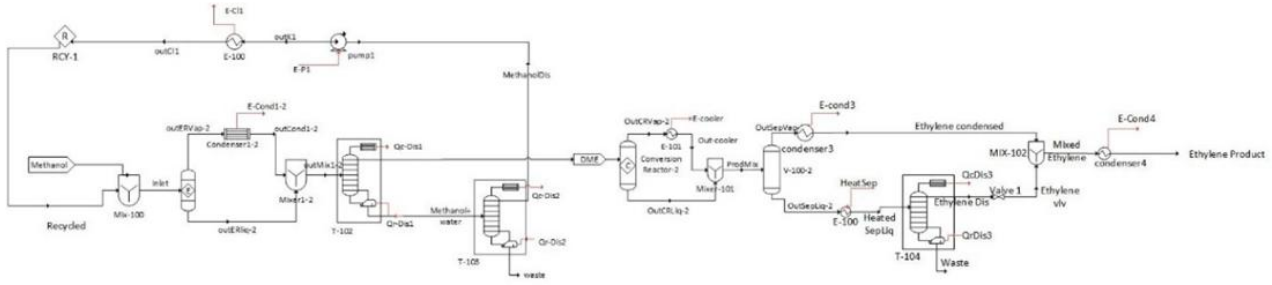

Figure 8. Process flow diagram of modified for ethylene production

[5] Gogate, M.R. (2019). Methanol-to-olefins process technology: current status and prospects. *Petroleum Science and Technology*, 37(5), 559-565. DOI: 10.1080/10916466.2018.1555589

[6] Xu, S., Zhi, Y., Han, J., Zhang, W., Wu, X., Sun, T., ... & Liu, Z. (2017). Advances in catalysis for methanol-to-olefins conversion. *Advances in Catalysis*, 61, 37-122. DOI: 10.1016/bs.acat.2017.10.002

[7] Kianfar, E., & Salimi, M. (2020). A review on the production of light olefins from hydrocarbons cracking and methanol conversion. *Advances in Chemistry Research,* 59, 1-81. DOI: 10.1515/revic-2019-0001

[8] Yu, B.Y., & Chien, I.L. (2016). Design and Optimization of the Methanol-to-Olefin Process. Part I: Steady-State Design and Optimization. *Chemical Engineering & Technology,* 39(12), 2293-2303. DOI: 10.1002/ceat.201500654

[9] Li, N., Zhao, L., Li, D., Sun, H., Zhang, D., & Liu, G. (2022). A simultaneous design and optimization framework for the reaction and distillation sections of methanol to olefins process. Processes, 11(1), 58. DOI: 10.3390/pr11010058

[10] Alshammari, A., Kalevaru, V.N., Bagabas, A., & Martin, A. (2016). Production of Ethylene and its Commercial Importance in the Global Market. In H. Al-Megren & T. Xiao (Editor), *Petrochemical Catalyst Materials, Processes, and Emerging Technologies*. IGI Global Scientific Publishing. DOI: 10.4018/978-1-4666-9975-5.ch004

[11] Mohammadi, R., & Hadizadeh Harandi, M. (2023). Methanol to Olefin (MTO) Value Chain Management. *New Applied Studies in Management, Economics & Accounting,* 6(1), 7-17. DOI: 10.22034/nasmea.2023.176134

[12] Amghizar, I., Vandewalle, L.A., Van Geem, K.M., & Marin, G.B. (2017). New trends in olefin production. *Engineering,* 3(2), 171-178. DOI: 10.1016/J.ENG.2017.02.006

[13] Kianinia, M., & Abdoli, S.M. (2021). Efficient Production of Light Olefin Based on Methanol Dehydration: Simulation and Design Improvement. *Combinatorial Chemistry & High Throughput Screening*, 24(4), 581-586. DOI: 10.2174/1386207323666200720104614.

[14] Rostami, R.B., Lemraski, A.S., Ghavipour, M., Behbahani, R.M., Shahraki, B.H., & Hamule, T. (2016). Kinetic modelling of methanol conversion to light olefins process over silicoaluminophosphate (SAPO-34) catalyst. Chemical Engineering Research and Design, 106, 347–355. DOI: 10.1016/j.cherd.2015.10.0

[15] Tan, H., & Cong, L. (2023). Modeling and Control Design for Distillation Columns Based on the Equilibrium Theory. *Processes*, 11(2), 607. DOI: 10.3390/pr11020607

[16] Ganesh, R.M., Manoharan, S., Marimuthu, C. N., & Senthil, J. (2021). Distillation Column-Modelling, Control and Optimization -A Review. *International Journal of Mechanical Engineering,* 6(3), 1123-1132. DOI: 10.1016/b978-0-12-802239-9.00016-5

[17] Fitriah, F., & Sari, D.A. (2023). Optimization of distillation column reflux ratio for distillate purity and process energy requirements. *International Journal of Basic and Applied Science*, 12(2), 72-81. DOI: 10.35335/ijobas.v12i2.260

[18] Xu, Y., Tang, Y., He, C., Shu, Y., Chen, Q.L., & Zhang, B.J. (2022). Internal coupling process of membrane/distillation column hybrid configuration for ethylene/ethane separation. *Chemical Engineering and Processing-Process Intensification*, 177, 108982. DOI: 10.1016/j.cep.2022.108982

[19] Moghaddam, H. (2022). A. Simulation and optimization of separation section in methanol to olefin (MTO) process based on statistical approach. *Chem. Pap*. 76, 4787–4794. DOI: 10.1007/s11696-022-02190-4

[20] Alshammari, A., Kalevaru, V.N., Bagabas, A., & Martin, A. (2016). Production of ethylene and its commercial importance in the global market. In *Petrochemical Catalyst Materials, Processes, and Emerging Technologies* (pp. 82-115). IGI Global. DOI: 10.4018/978-1-4666-9975-5.CH004

[21] Karimi, A., Soltani, H., & Hasanzadeh, A. (2020). An analysis of increasing the purity of ethylene production in the ethylene fractionation column by the genetic algorithm. *Chemical Product and Process Modeling*, 15(3), 20190088. DOI: 10.1515/cppm-2019-0088

[22] Chen, Y., Kuo, M.J., Lobo, R., & Ierapetritou, M. (2024). Ethylene production: process design, techno-economic and life-cycle assessments. *Green Chemistry*, 26 (5), 2903-2911. DOI: 10.1039/d3gc03858k

[23] Treger, Y.A., & Rozanov, V.N. (2016). Technologies for the synthesis of ethylene and propylene from natural gas. *Review Journal of Chemistry,* 6 (1), 83-123. DOI: 10.1134/S2079978016010039

[24] Leonzio, G., Chachuat, B., & Shah, N. (2023). Towards ethylene production from carbon dioxide: Economic and global warming potential assessment. *Sustainable Production and Consumption,* 43, 124-139. DOI: 10.1016/j.spc.2023.10.015

[25] Bhusal, S.R. (2021). Carbon footprint of polyethylene produced from CO_2 and renewable H_2 via MTO route. *Master's Thesis*, Department of Environmental Technology, Lappeenranta–Lahti University of Technology.