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RESEARCH ARTICLE

Efficient Production of Light Olefin Based on Methanol Dehydration: Simulation and Design Improvement

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Abstract: ***Background:*** Ethylene, propylene, and butylene as light olefins are the most important intermediates in the petrochemical industry worldwide. Methanol to olefins (MTO) process is a new technology based on catalytic cracking to produce ethylene and propylene from methanol.

Aims and Objective: This study aims to simulate the process of producing ethylene from methanol by using Aspen HYSYS software from the initial design to the improved design. ***Methods:*** Ethylene is produced in a two-step reaction. In an equilibrium reactor, the methanol is converted to dimethyl ether by an equilibrium reaction. The conversion of the produced dimethyl ether to ethylene is done in a conversion reactor. Changes have been made to improve the conditions and get closer to the actual process design performed in the industry. The plug flow reactor has been replaced by the equilibrium reactor, and the distillation column was employed to separate the dimethyl ether produced from the reactor.

Result and Conclusion: The effect of the various parameters on the ethylene production was investigated. Eventually, ethylene is produced with a purity of 95.5 % in the improved design, and thermal integration was performed to minimize energy consumption.

Keywords: Methanol, light olefin, ethylene, simulation, process design, aspen HYSYS.

1. INTRODUCTION

The most common olefins considered to be essential components of the chemical industry are ethylene and propylene. These components annually are produced approximately 1.5×10^8 t and 8×10^7 t, respectively [1], which are used as the feedstock in the production of a wide variety of chemicals, including polymers (e.g., polyethylene), oxygenates (e.g., ethylene glycol), and significant chemical intermediates (e.g., ethylbenzene) [2, 3]. Nevertheless, the global demand for these compounds has risen considerably in recent years [4].

There are currently three major processes to produce olefins, including steam hydrocarbon cracking (naphtha, ethane, gas oil, and LPG), fluid catalytic cracking in oil refineries, and paraffin dehydrogenation. Virtually, all ethylene and about 70% of the world's propylene are produced by steam cracking [5]. Extensive research is, therefore, being done to achieve the technologies for the direct production of light olefins, particularly from non-oil sources [6, 7]. Oxidative coupling of methane and methanol to olefins (MTO) process are some new technologies under various phases of development [8].

Methanol to olefin (MTO) process has some advantages over the conventional ethylene and propylene production process. This process provides a wide range of ethylene to propylene ratio based on market demands [9]. Methanol is widely used in the chemical industries as a feedstock, fuel or solvent. It is conventionally produced through the conversion of syngas under high pressure and temperature, whereas it can be derived from various feedstock such as coal, petroleum residues, biomass, and natural gas [10]. At the moment, the direct conversion of these resources to the light olefins seems to be complicated or inefficient. Therefore, methanol can also be considered as an essential intermediate for the production of ethylene and propylene [11].

Several institutions and companies have made significant efforts to investigate the MTO reaction. Focused on the reaction principle, synthesis of catalyst, and process research and development, substantial advancements have been made in this field [12, 13]. A new technology developed by UOP/Norsk Hydro converts methane to methanol firstly, and then the methanol into olefins. Economically, this technology tends to be competitive with conventional processes [14]. The MTO technology has been well

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developed and established in China, which has led to a successful start of the first MTO plant in the world [12]. Copper/zinc oxide catalysts are used mainly in the methanol production process [10]. Once the methanol is partially converted into an intermediate product (dimethyl ether), then ethylene over SAPO-34 or ZSM-5 catalysts is produced [15, 16].

The thermodynamic analysis allows the reaction network to be realized in the first step, which is hugely significant. The thermodynamic properties of the reactions calculated at a standard temperature of 298°C are given in Table **1**. For each reaction, Gibbs free energy was measured as a function of temperature (50-850°C), with a focus on the predicted industrial temperature range of 300-500°C. Due to the negative ΔG, it was found that both reactions are thermodynamically feasible [17].

Table 1. Thermodynamic properties of reactions in MTO process.

NO*	Reaction	ΔH°	ΔG°
		(kJ.mol^{-1})	(kJ.mol^{-1})
R_1	$2CH_3OH \rightarrow CH_3OCH_3+H_2O$	-22.57	-16.19
R_2	$CH_3OCH_3 \rightarrow C_2H_4+H_2O$	-6.42	-48.02

***R_1:** Methanol to DiMethyl Ether (DME), **R_2:** DME to Olefin.

Among the extensive research, Pyl et al. proposed an alternative route for light olefins production [18]. In this method, low value and waste fats, greases, and other renewable fractions are used as raw materials to produce a high quality paraffinic diesel or jet fuel and renewable naphtha. Xiang et al. suggested a method to reduce the oil and natural gas consumption in olefin production [19]. They used coal as an alternative natural source to produce olefins. The findings showed that the coal-based olefins process is more cost-effective. Onel et al. utilized biomass and natural gas to produce liquid fuels and olefins simultaneously [20]. Through their work, they applied a process synthesis and global optimization. The results showed that high olefin production would make the plant more competitive from an economic perspective. Arvidsson *et al.* studied the thermodynamic efficiency of alternative platform chemicals for light olefin production by lignocellulosic biomass gasifying [21]. Two methods that include methanol synthesis and DME synthesis are evaluated for olefins production. The result indicates that direct DME synthesis can overcome the thermodynamic equilibrium constraint present in methanol synthesis. Compared to the conventional approach for producing olefins by steam cracking, Yu et al. simulated a more economical and steady-state design of the MTO process [22]. Results revealed that the new design has a more extensive range of ethylene to propylene ratio, suitable reaction condition, and higher selectivity. Ortiz- Espinoza et al. simulated ethylene production from shale gas with two methods based on methanol to olefins and oxidative coupling of methane (OCM) process [23]. Economic analysis was examined, and the results showed that the MTO process had a higher return on investment value than the OCM process.

Despite extensive studies in the explained research field, the challenge remains to simulate and determine the effect of key operation parameters on ethylene production in the MTO process. The objective of the present work is a simulation of the MTO process based on the intermediate product (dimethyl ether) and a survey of critical operating parameters effects.

2. SIMULATION METHODOLOGY

This study relies on using Aspen HYSYS 10.1, which is a commercial process simulator [24]. All input and output components involved in the MTO process, including methanol, dimethyl ether, ethylene, and water, were selected from Aspen HYSYS pure components databank and added to the component list. The nonrandom two-liquid (NRTL) model was chosen as an appropriate thermodynamic fluid package, and two sets of MTO process reactions were specified. Set 1 includes the equilibrium reaction (R_1), which results in the production of dimethyl ether and water from methanol in an equilibrium reactor. The conversion of dimethyl ether to ethylene and water in a conversion reactor is done by set 2 (R_2). The dimethyl ether conversion value is set to 95%. A feed stream consists of methanol that flows at 70°C and 101.325 kPa to the equilibrium reactor with a flow rate of 875 kmol/h. The process flow diagram (PFD) for the ethylene production process, generated by the Aspen HYSYS, is shown in Fig. (**1**).

3. RESULTS AND DISCUSSION

According to simulation results, the conversion of methanol in the equilibrium reactor and the purity of ethylene produced were 88.4% and 29.63%, respectively. Therefore, all the parameters influencing the ethylene production process were explored to improve the conditions and to get closer to the actual process design performed in the industry. Simulation makes it possible to assess the effect of installing equipment or modifying usable and logical operational conditions. In this regard, three scenarios are considered below.

3.1. Using the Plug Flow Reactor

The plug reactor is replaced with an equilibrium reactor to get more practical and industrial results. The reaction kinetics information is needed to run the plug flow reactor. Activation energy and pre-exponential factor of methanol to dimethyl ether reaction were obtained from Rostami et al. [25] and are given in Table **2**. In addition, the SAPO-34 catalyst characteristics used in the plug reactor are provided in Table **3** [16].

The reaction set 1 was selected after the appropriate information has been entered. The effect of methanol feed temperature was investigated for four temperatures at different pressures. As shown in Fig. (**2**), preheating the feed stream and increasing the temperature raises the dimethyl ether. The findings are in good agreement with the experimental data [25], indicating that the reactor's optimal temperature range for converting methanol to dimethyl ether is 400 to 460°C. Fig. (**2**) also shows that the production rate can be altered by changing the pressure. Pressure rise can increase the production rate to the extent that methanol is wholly involved in all active sites of the catalyst particles.

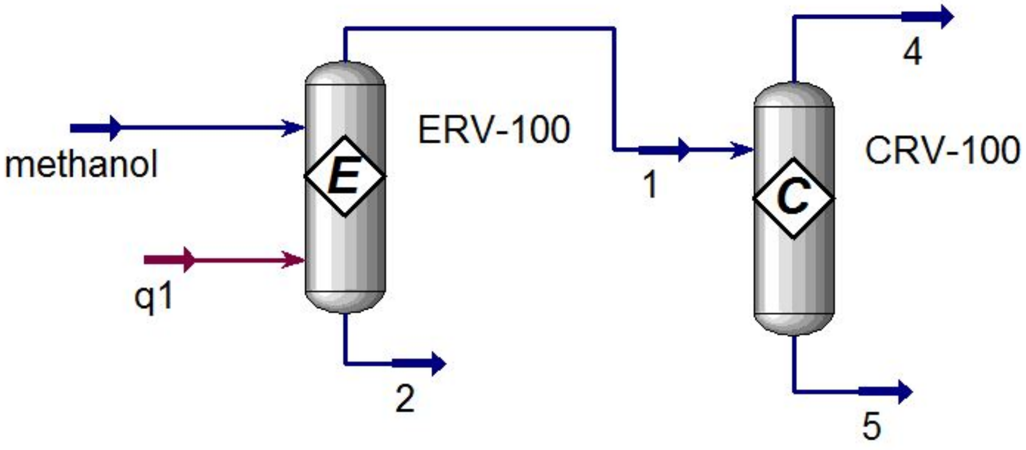

Fig. (1). PFD of ethylene production process (initial design).

Table 2. Activation energy and pre-exponential factor of methanol to dimethyl ether reaction.

k_i° (mole/$g_{catalyst}$.atm.hr)	**17.322**
E_i (kJ/mole)	52.51

Table 3. Characteristics of SAPO-34 catalyst.

Average diameter of catalyst particles (m)	8×10^{-5}
Catalyst density (kg/m^3)	1500
Catalyst heat capacity (kJ/kg.K)	1.003
Void fraction (-)	0.55

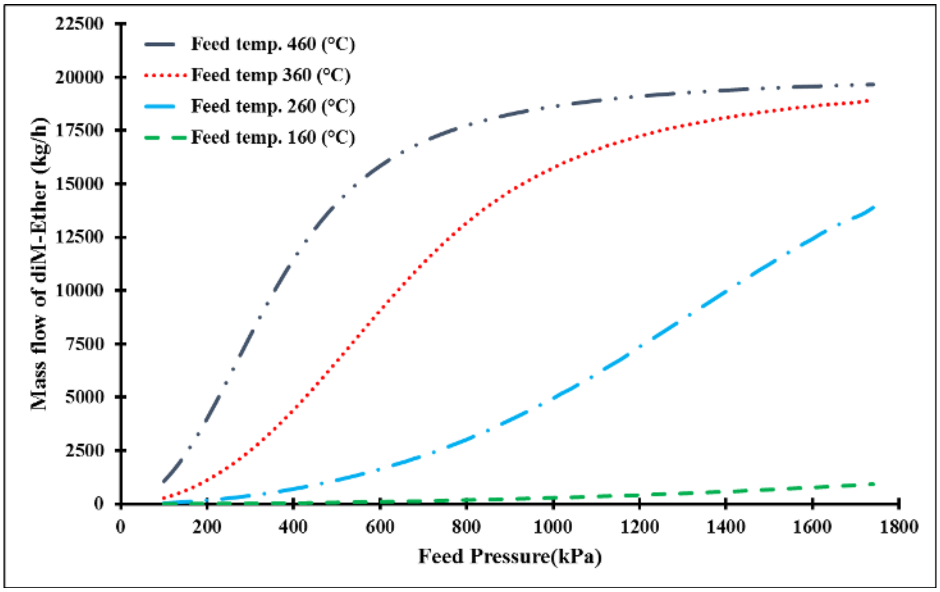

Fig. (2). Effect of methanol feed temperature and pressure on diM-Ether production rate.

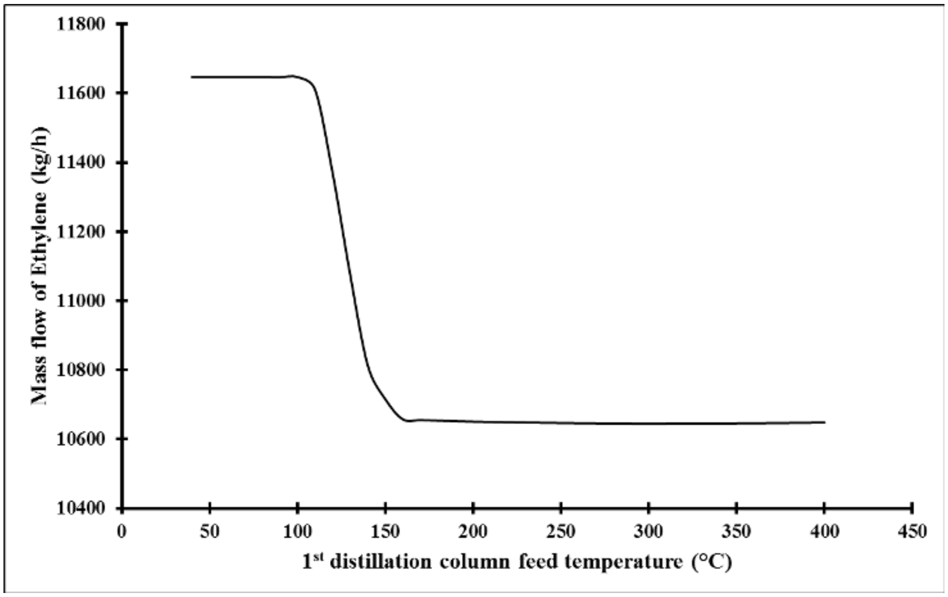

Fig. (3). Effect of first distillation column feed stream temperature on ethylene production.

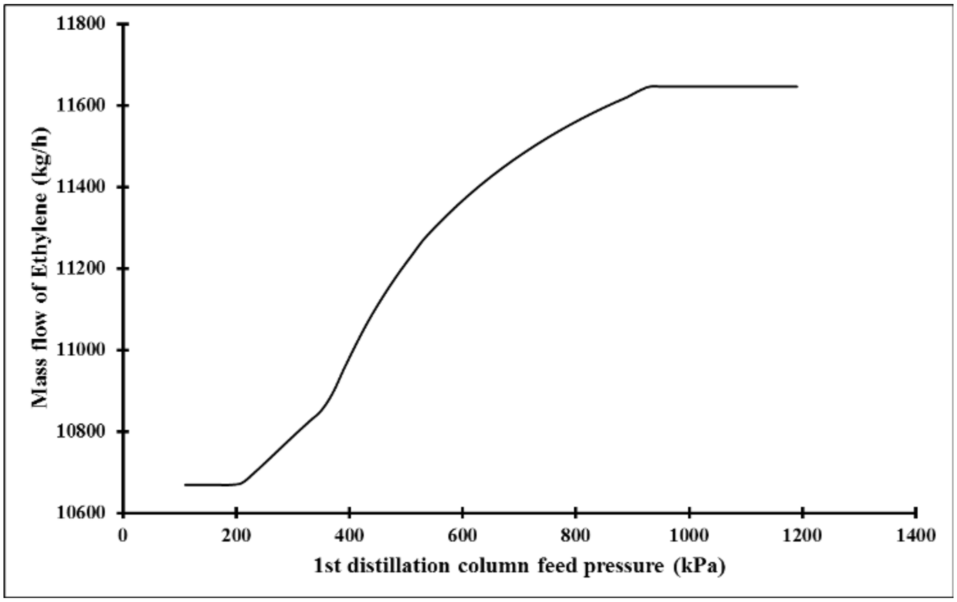

Fig. (4). Effect of first distillation column feed stream pressure on ethylene production.

As it can be seen from Fig. (**2**), dimethyl ether production reaches its highest value at 1200 kPa, and no significant changes are observed at higher pressures. Thus, the pump and heater must be used to increase the pressure and temperature of methanol to 1200 kPa and 460°C, respectively.

3.2. Using Distillation Columns

Production of plug reactor includes dimethyl ether, unreacted methanol, and water. Pure dimethyl ether is required to produce ethylene according to reaction 2 (R_2). Dimethyl ether is separated by using the first distillation column; the bottom stream of the tower contains methanol and water. To improve plant efficiency and reducing feed consumption, methanol can be separated from water in the second distillation column.

The first and second distillation columns consist of 20 and 30 stages (trays), respectively. Effective parameters such as feed temperature and pressure, and reflux ratio have been investigated to increase the amount of ethylene produced. The effect of the first distillation column feed stream on ethylene production is shown in Fig. (**3**). It can be observed that the maximum production of ethylene is available at a temperature of 100°C. In the distillation column feed zone, excessive the feed temperature rise can cause a considerable flash of heavy key and non-key components, so separation efficiency is not always improved. As the temperature of the reactor outlet stream is 554.8°C, it needs a cooler to cool the inlet stream to the desired temperature.

Fig. (**4**) demonstrate the effect of first distillation column feed pressure on ethylene production. Through increasing the pressure, heavier components in the distillate product are decreasing. It can be found that the amount of ethylene production has increased with rising pressure. The maximum amount of ethylene produced in 930 kPa is readily visible, and more pressure has little effect on ethylene production. The pressure of the reactor's output stream is 1150 kPa, and it requires a control valve to reduce to the optimal level. The distillation column reflux ratio changes the purity of the products. The influence of the first distillation column reflux ratio on ethylene production is illustrated in Fig. (**5**). This figure shows that a high reflux ratio leads to more ethylene production. As can be deduced, the ethylene mass flow can achieve its maximal value with a reflux ratio of 0.8; and the impact of any further rise is slight.

The top stream of the first distillation column, which contains only dimethyl ether, is sent to a conversion reactor and converted to ethylene and water (by-product). After cooling, the output stream from the conversion reactor is sent to a separator to achieve high purity ethylene. Improving the design of the ethylene production process leads to 95.5% purity of the produced ethylene, which is nearly three times more than the previous design described in the last section. Fig. (**6**) displays the improved design of the ethylene production process.

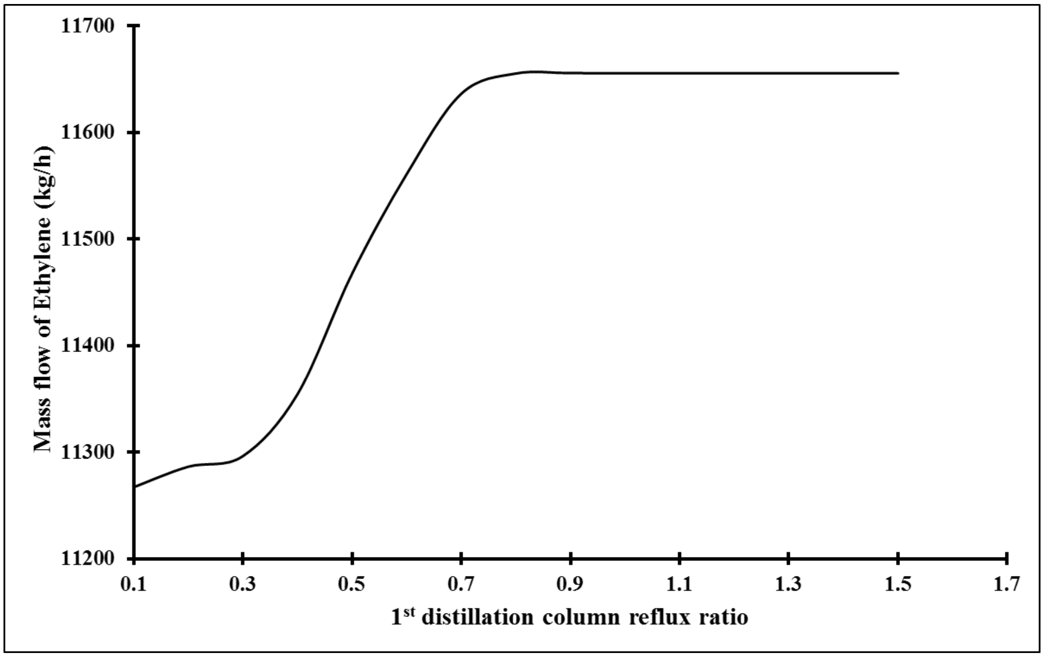

Fig. (5). Effect of first distillation column reflux ratio on ethylene production.

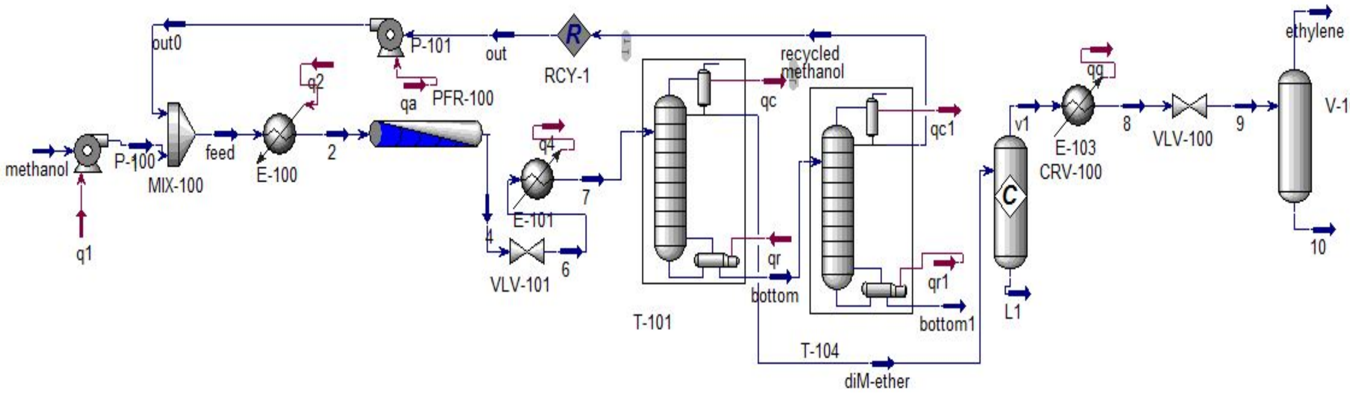

Fig. (6). Improved design of ethylene production process.

3.3. Thermal Integration

A general energy analysis of the integrated system was carried out to determine the most cost-effective thermal integration method. As discussed before, the feed stream should be heated to 460°C before the plug flow reactor to achieve maximum conversion. Due to the exothermic reaction of the production of dimethyl ether from methanol, the temperature of the output stream from the reactor rises to 565°C. Finally, the separator production had to be cooled to 100°C. As a result, the energy used in the heater and cooler were 6.044×10^4 MJ/h and 5.522×10^4 MJ/h respectively to heat and cool the flow. Hence, according to the temperature of the output stream of the reactor, it can be used to heat the reactor input. Using the shell and tube heat exchanger in the simulation environment and applying thermal integration, it was noticed that the duty of the heater and cooler decreased by 18.5% and 26.5%, respectively. In terms of energy

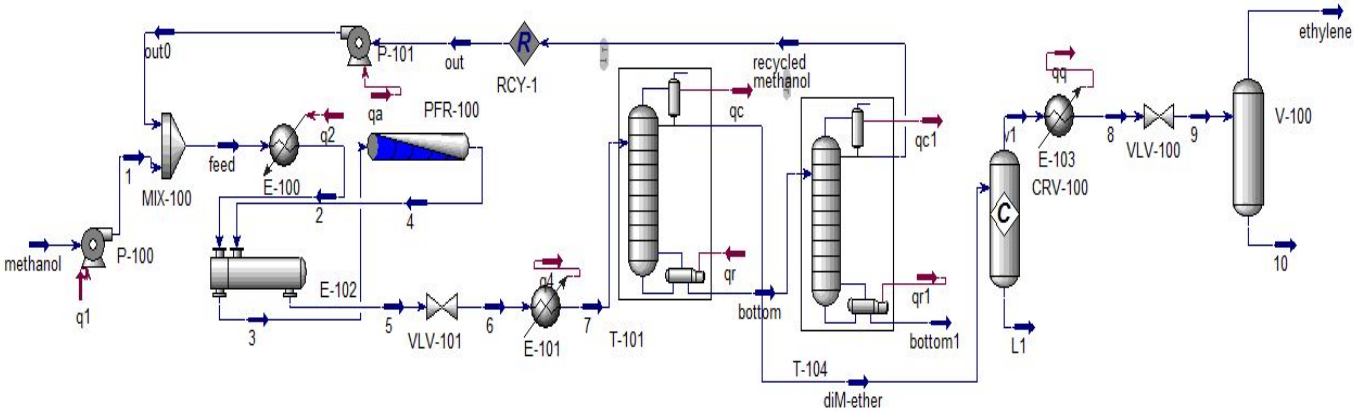

Fig. (7). PFD of ethylene production process with thermal integration.

optimization, the results revealed that using the energy of process streams and thermal integration reduces energy consumption and costs. The PFD of the ethylene production process with thermal integration is shown in Fig. (**7**).

CONCLUSION

Due to the application and importance of light olefins, especially ethylene, in the oil industry through out the world, the production process was simulated by Aspen HYSYS software. By performing all operations to improve the production situation, the results showed that the material balance around each of the equipment had been established, and ethylene can be produced with a purity of 95.5% from methanol. The effect of key operating parameters on the production of the desired product, including the first distillation column feed temperature and pressure, and the reflux ratio of the first column were investigated. The results showed that the most appropriate conditions for the feed stream of the first distillation column were 100°C, and 930 kPa, and the best reflex ratio was 0.8. It was finally found according to the exothermic reaction of the dimethyl ether production, thermal integration in the process reduces the energy consumption in the heater and cooler.

HUMAN AND ANIMAL RIGHTS

Not applicable.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

Not applicable.

FUNDING

None.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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Declared none.

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