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DESIGN OF A METHANOL-TO-OLEFIN PROCESS USING ASPEN HYSYS: MATERIAL AND ENERGY BALANCES

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ABSTRACT

This work is aimed at carrying out the simulation of a process designed for the production of olefin from methanol with the aid of Aspen HYSYS. The olefin considered in this work was ethylene, which was synthesised in two steps: (1) equilibrium conversion of methanol to dimethyl ether using an equilibrium reactor, and (2) conversion of the produced dimethyl ether to ethylene. General Non-Random Two-Liquid (NRTL) model was employed as the Fluid Package of the simulation. The results obtained showed that a conversion of up to 98.29% was feasible for the reaction involving production of dimethyl ether from methanol. Moreover, the simulation of the design model with the aid of Aspen HYSYS showed that it (the model) was a valid one because the results were found to be in good agreement with the theoretical principles of the process in each piece of equipment used. Furthermore, the material flow given by Aspen HYSYS around each of the pieces of process equipment were found to be balanced because the total amount of input for each component was equal to that of the output, in a situation where there was neither consumption nor generation. Also, the energy balances across the pieces of equipment of the process indicated that the all the process equipment of the design were having negligible heat duties except the condensers.

Keywords: methanol, olefin, modelling, design, simulation, Aspen HYSYS.

1. INTRODUCTION

Synthesis of light olefin has attracted a tremendous attention during the past few years in an attempt to meet up with the increasing worldwide demand towards ethylene. Nowadays, the interest in obtaining light olefins is increasing because they are important petrochemical feed stocks [1-4]. Not only for ethylene, but a large increase in demand for both ethylene and propylene is expected to occur in the future. At present, most light olefins are obtained from thermal cracking of naphtha, and this is a very energy consuming and expensive process. Alternatively, light olefins can be produced using natural gas as the feedstock because direct production of light olefins from natural gas is a possible production route. However, pyrolysis of methane to olefins is very energy demanding, and the yield obtained from that process is very low. Another alternative route of olefin production is oxidative coupling of methane over oxide catalysts in which the olefin yields are also very low. However, indirect production of olefins from natural gas, through the production of methanol, seems to be a possible olefin production route from which high yields can be obtained [5-6].

The methanol-to-olefins (MTO) process for light olefins synthesis came up from the development of methanol-to-gasoline (MTG) process, as a supplementary route to obtaining synthetic gasoline [7-9]. Originally, the interest of this process was upgrading of a raw material alternative to oil (biomass, coal, natural gas) via methanol synthesis [1-4].

Alternative processes for the production of olefins, and other hydrocarbons, from non-petroleum sources without using a large amount of energy have been steadily studied [10-11]. Table-1 gives the summary of some researches already carried out concerning this process.

Table-1. Summary of past researches carried out on conversion of methanol to hydrocarbons.

S. No	Author(s)	Year	Title	Material and operating parameters
	Bjørgen and Kolboe [12]	2002	The Conversion of Methanol to Hydrocarbons over Dealuminated Zeolite H-beta	Reactor: Fixed bed Pyrex micro reactor Temperature: 400 ^{o}C Catalyst: Dealuminated zeolite H-beta Feed: Methanol
	Bjørgen et al. [13]	2007	Conversion of Methanol to Hydrocarbons over Zeolite H-ZSM-5:On the Origin of the Olefinic Species	Reactor: Fixed bed Pyrex reactor Temperature: 290 - 390 ^{o}C Catalyst: Zeolite H-ZSM-5 Feed: >99.8% Methanol
	Campbell et al. [14]	1999	Methanol to Hydrocarbons: Spectroscopic Studies and theSignificance of Extra-Framework Aluminium	Reactor: Pulsed microreactor Temperature: 423 K Catalyst: HZSM-5 Feed: Methanol
	Dewaele et al. [15]	1999	The Conversion of Methanol to Olefins: a Transient Kinetic Study	Reactor: TAP reactor system Temperature: 623-773 K Pressure: 100 kPa Catalyst: H-ZSM-5 zeolite Feed: Methanol
	Freeman et al. [16]	2002	Conversion of Methanol to Hydrocarbons over Ga_2O_3/H-ZSM-5and Ga_2O_3/WO_3 Catalysts	Reactor: Stainless-steel microreactor Temperature: <, = and > 400 ^{o}C Catalyst: Ga_2O_3/H-ZSM-5 and Ga_2O_3/WO_3 Feed: Methanol
	Masuda et al. [17]	2003	Methanol to Olefins using ZSM-5 Zeolite Catalyst Membrane Reactor	Reactor: Catalyst membrane reactor Temperature: 673 K Catalyst: ZSM-5 zeolite Feed: Methanol
	Mikkelsen and Kolboe [18]	1999	The Conversion of Methanol to Hydrocarbons over Zeolite H-beta	Reactor: Fixed-bed quartz microreactor Temperature: 400 °C Pressure: 150 mbar Catalyst: H-beta zeolite Feed: > 99.8% methanol
	Travalloni et al. [19]	2008	Methanol Conversion over Acid Solid Catalysts	Reactor: Pyrex tubular reactor Temperature: 450 ^{o}C Pressure: Atmospheric pressure Catalyst: SAPO-34 Feed: Methanol
	Tsoncheva and Dimitrova [20]	2002	Methanol Conversion to Hydrocarbons on Porous Aluminosilicates	Reactor: Fixed bed reactor Temperature: Above 550 K Pressure: Atmospheric pressure Catalyst: Aluminosilicates Feed: Methanol
	Zhu et al. [21]	2008	The study of Methanol-to-Olefin over Proton TypeAluminosilicate CHA Zeolites	Reactor: Plug flow reactor Temperature: 598 K Pressure: Catalyst: Proton-type aluminosilicate H/CHA zeolites Feed: 6.1% methanol diluted in N_2
	Zhu et al. [22]	2008	Methanol-to-Olefin over Gallosilicate Analogues of Chabazite Zeolite	Reactor: Fixed bed reactor Temperature: 598 K Catalyst: Gallosilicate analogues of chabazite zeolite with CHA topology Feed: Methanol

As can be seen from the literature review summarized in Table-1, most of the researches carried out on the conversion of methanol to olefins have been on experimental basis. Researches on the subject matter involving design in the form of modelling and simulation using process simulators have been discovered to be very

scarce in the literature. This has been observed to be a gap, and it is the aim of this work to bridge this gap. Therefore, this work is carried out to use Aspen HYSYS in carrying out the material and energy balances of olefin synthesis from methanol. The olefin considered in this work was ethylene.

2. METHODOLOGY

The procedures employed to accomplish this research work involving the design of a process for methanol-to-olefin synthesis with the aid of modelling and simulation carried out using Aspen HYSYS are as outlined below.

2.1 Selection of process components

The components, both inputs and outputs, which were methanol, dimethyl ether, ethylene and water, involved in the process were selected from the Pure Components Databank of the Aspen HYSYS and added to the Component List.
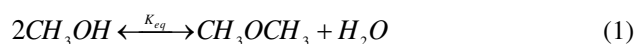
2.2 Selection of fluid package

After the components were selected from the Databank of Aspen HYSYS, the Fluid Package that was used to estimate the properties of the components was also selected from Aspen HYSYS Databank. The Fluid Package used in this work was selected to be General NRTL (Non-Random Two-Liquid) model. After selecting the General NRTL as the Fluid Package, the binary

coefficients required for the property estimation were automatically generated by the process simulator.

2.3 Development of methanol-to-olefin reaction

After selecting the components and the fluid package for the process, the reactions involved in the process were developed in two sets. Reaction Set 1 contained the equilibrium reaction involving the production of dimethyl ether and water from methanol (Equation 1) while Reaction Set 2 contained the conversion of dimethyl ether to ethylene and water (Equation 2). The conversion value of the reaction given in Equation 2 was taken to be 95%.

$$2CH_3OH \xleftrightarrow{K_{eq}} CH_3OCH_3 + H_2O \qquad (1)$$

$$CH_3OCH_3 \rightarrow C_2H_4 + H_2O \qquad (2)$$

The two reaction sets developed were attached to the selected Fluid Package, which was General NRTL before being used in the Simulation Environment of the Aspen HYSYS.

2.4 Development of process flow sheet

After all the procedures outlined above had been carried out, the Simulation Environment of the Aspen HYSYS was entered and the flow sheet of the process was developed as shown in Figure-1.
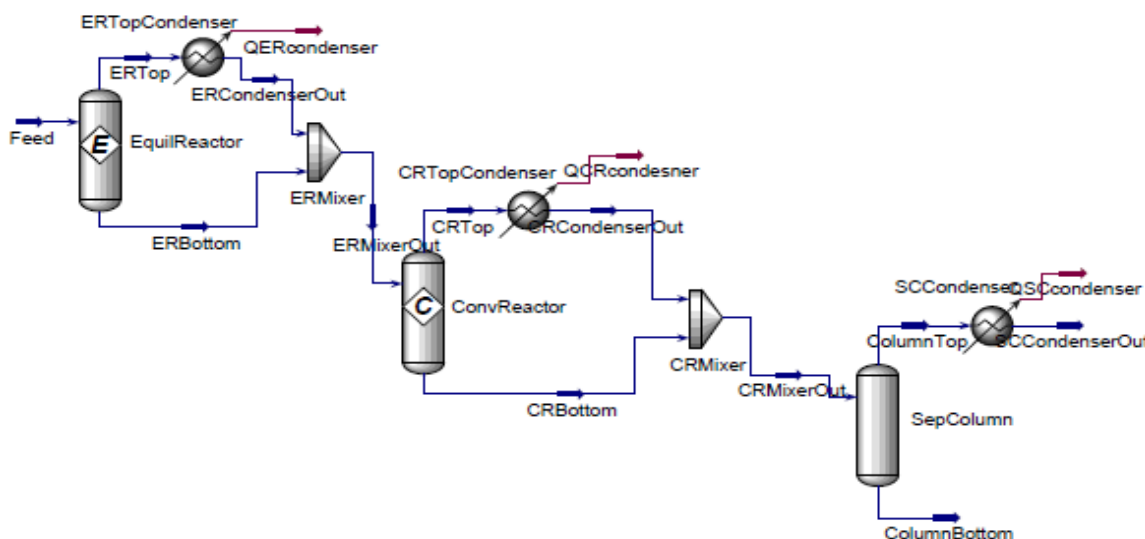

Figure-1. Process flow sheet for the design of methanol-to-ethylene process.

The development of the flow sheet was accomplished by picking the pieces of equipment from the Model Palette of the Aspen HYSYS and connecting them together appropriately. The reactors were picked from the "Column" section while the cooler and the mixer were taken from the "Common" section of the Palette.

After developing the flow sheet as described above, it was simulated using 30 mL/min (0.7450 gmol/min) of methanol at a temperature of 25 °C and a pressure of 1 atm as the feed to the equilibrium reactor.

The vapour leaving the top of the reactor, which was containing dimethyl ether, water and unreacted methanol, was condensed by setting its vapour fraction to zero in order to become liquid before being mixed with the liquid, which was also containing dimethyl ether, water and unreacted methanol, exiting the bottom section of the reactor. The resulting mixture was then passed into a conversion reactor where the dimethyl ether was converted to ethylene giving water as the by-product of the process. The vapour leaving the top section of the conversion

reactor also was cooled to become liquid and mixed with the liquid leaving the bottom of the reactor. Thereafter, the resulting liquid mixture was fed into a separator so as to obtain high purity of the desired product, which was ethylene, and this aim was achieved with the separation operation. The desired product was observed to leave as vapour from the top section of the separator, and it was converted to liquid product for storage and further use in the industries.

3. RESULTS AND DISCUSSIONS

The results obtained from the simulation carried out showed that a conversion of up to 98.29% with an equilibrium constant of 893.00 could be achieved in the equilibrium reactor in which the production of dimethyl ether and water as a by-product from methanol took place. The value obtained for the conversion of the methanol to dimethyl ether was observed to be very good in favour of

the process as relatively enough dimethyl ether was generated to be used for ethylene synthesis.

Apart from considering the reaction conversion and equilibrium constant of the process, the balances around each of the pieces of process equipment were as well analysed, and given in the subsequent subsections are the results of the analyses of the balances.

3.1 Balances around equilibrium reactor

Table-2 shows the operating conditions and the flow of energy around the equilibrium reactor in which the generation of dimethyl ether from of methanol was taking place. Based on the results given in Table-2, the feed, which was the methanol fed into the reactor, was liquid because its vapour fraction was zero. Also, it was discovered from the results that both vapour and liquid products were exiting the reactor at the same temperature and pressure. However, the amount of liquid product was more than that of the vapour product.

Table-2. Operating conditions and energy flow of the equilibrium reactor.

Name	Input	Top output	Bottom output
Vapour Fraction	0.00	1.00	0.00
Temperature [^{o}C]	25.00	9.76	9.76
Pressure [atm]	1.00	1.00	1.00
Molar Flow [gmol/min]	0.75	0.22	0.52
Mass Flow [g/min]	23.87	10.29	13.58
Liquid Volume Flow [mL/min]	30.00	15.33	16.96
Heat Flow [kJ/min]	-178.38	-41.72	-136.66

Also noticed from the results given in Table-2 was that the heat flow for all the streams were negative, although the total heat load around the equilibrium reactor

was estimated to be 0 kJ/min. Furthermore, the reaction itself was found to exothermic because its heat of reaction at 25 ^{o}C was estimated to be -1.17E+04 kJ/kmol.

Table-3. Molar flow rates of the components around the equilibrium reactor.

Component	gmol/min		
	Input	Top output	Bottom output
Methanol	0.7450	0.0007	0.0120
Dimethyl ether	0.0000	0.2221	0.1440
Water	0.0000	0.0019	0.3643
Ethylene	0.0000	0.0000	0.0000

The results given in Table-3 shows the molar flow rates of the components involved in the process for the equilibrium reactor. According to the results, the amount of each component entering the reactor was found not to be the same with the amount leaving. This was observed to be due to the occurrence of a chemical reaction, in which there were consumption and generation, in the equilibrium reactor. This observation was found to be one of the reasons to say that the developed Aspen HYSYS model for the design of the process was functioning properly.

3.2 Balances around equilibrium reactor top product condenser

The operating conditions and energy flow around the condenser of the equilibrium reactor were as given in Table-4. As expected, the material entering the condenser was vapour, as its vapour fraction was 1, while the one leaving was liquid with a vapour fraction of 0. It can be noticed from the results that, though the pressures of both the input and the output of the condenser were the same, their temperatures were different.

Table-4. Operating conditions and energy flow of the equilibrium reactor top product condenser.

Name	Input	Output
Vapour Fraction	1.00	0.00
Temperature [^{o}C]	9.76	-24.55
Pressure [atm]	1.00	1.00
Molar Flow [gmol/min]	0.22	0.22
Mass Flow [g/min]	10.29	10.29
Liquid Volume Flow [mL/min]	15.33	15.33
Heat Flow [kJ/min]	-41.72	-47.08

It was also discovered from the results given in Table-4 that as the temperature of the output was less than that of the input of the condenser, the heat flow of the former was also less than that of the latter. This was showing some heat has been lost to be able to convert the vapour to liquid, and this was in line with the basic principle of condensation. That was another point showing the validity of the developed Aspen HYSYS model of the process.

Table-5. Molar flow rates of the components around the equilibrium reactortop product condenser.

Component	gmol/min	
	Input	Output
Methanol	0.0007	0.0007
Dimethyl ether	0.2221	0.2221
Water	0.0019	0.0019
Ethylene	0.0000	0.0000

Table-5 gives the material flow of the components of the process. As there was not any material exchange in the condenser, the amount of each component entering the condenser was found to be equal to the amount leaving it.

3.3 Balances around equilibrium reactor products mixer

The results obtained from the simulation for the balances around the mixer, which was used to combine the condensed liquid and the liquid given from the bottom of the reactor, are given in Table-6. It was observed from the results that both inputs to the mixer were liquid in nature while the output was also approximately liquid at atmospheric pressure. Also observed from Table-6 was that the total heat of the inputs and that of the output were the same as, in the mixer, there was not any heat exchange; only material change was involved.

Table-6. Operating conditions and energy flow of the equilibrium reactor products mixer.

Name	Top input	Bottom input	Output
Vapour Fraction	0.00	0.00	0.02
Temperature [^{o}C]	-24.55	9.76	-6.36
Pressure [atm]	1.00	1.00	1.00
Molar Flow [gmol/min]	0.22	0.52	0.75
Mass Flow [g/min]	10.29	13.58	23.87
Liquid Volume Flow [mL/min]	15.33	16.96	32.29
Heat Flow [kJ/min]	-47.08	-136.66	-183.74

Table-7. Molar flow rates of the components around the equilibrium reactor products mixer.

Component	gmol/min		
	Top input	Bottom input	Output
Methanol	0.0007	0.0120	0.0127
Dimethyl ether	0.2221	0.1440	0.3661
Water	0.0019	0.3643	0.3661
Ethylene	0.0000	0.0000	0.0000

The results obtained as the molar flow rates of the components in the mixing of the products of the

equilibrium mixer were obtained as given in Table-7. The results indicated that there were correct component material balances because the summation of the components in the two input streams gave the values of the components in the output stream.

3.4 Balances around conversion reactor

Now, passing the output of the equilibrium reactor mixer into another reactor for the conversion of the dimethyl ether into ethylene, the results obtained for the operating conditions and energy balances are given in Table-8. From the results, it was found out that while the input was approximately liquid in nature because its vapour fraction was 0.02, the top output of the conversion reactor was total vapour but the bottom one was liquid.

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However, the volumetric flow rate of the top product was observed to be far more than that of the bottom product of

the conversion reactor.

Table-8. Operating conditions and energy flow of the conversion reactor.

Name	Input	Top output	Bottom output
Vapour Fraction	0.02	1.00	0.00
Temperature [^{o}C]	-6.36	63.90	63.90
Pressure [atm]	1.00	1.00	1.00
Molar Flow [gmol/min]	0.75	0.49	0.61
Mass Flow [g/min]	23.87	12.84	11.03
Liquid Volume Flow [mL/min]	32.29	29.00	11.13
Heat Flow [kJ/min]	-183.74	-12.99	-170.75

Table-9 gives the results obtained from the material balances around the conversion reactor. It was observed from the results that the molar flow rates of the components involved in the conversion reaction, which were dimethyl ether, water and ethylene, that were in the input were not the same with those in the output. However, the molar flow rate of the methanol in the input was estimated to be the same as the total amount of methanol leaving the reactor, which was calculated by summing the methanol in the top and the bottom outputs of the reactor. The reasons for this were due to the consumption and generation occurring inside the reactor.

Table-9. Molar flow rates of the components around the conversion reactor.

Component	gmol/min		
	Input	Top Output	Bottom Output
Methanol	0.0127	0.0081	0.0046
Dimethyl ether	0.3661	0.0169	0.0014
Water	0.3661	0.1132	0.6008
Ethylene	0.0000	0.3478	0.0000

3.5 Balances around conversion reactor top product condenser

The vapour product leaving the top of the conversion reactor was also condensed, and the results obtained from the condensation operation are given in Tables 10 and 11.

Table-10 gives the operating conditions as well as the energy flow of the condenser. From the results, it was discovered that the vapour fraction of the condenser output was 0 because the vapour entering it, which had a vapour fraction of 1, had been turned into liquid at atmospheric pressure but different temperature from that of the input. The difference in the temperatures of input and that of the output of the condenser resulted in the difference in the heat flow around the condenser, and this made the heat flow of the output of the condenser to be less than that of

its input. This was an indication of heat loss around the condenser.

Table-10. Operating conditions and energy flow of the conversion reactor top product condenser.

Name	Input	Output
Vapour Fraction	1.00	0.00
Temperature [^{o}C]	63.90	-123.49
Pressure [atm]	1.00	1.00
Molar Flow [gmol/min]	0.49	0.49
Mass Flow [g/min]	12.84	12.84
Liquid Volume Flow [mL/min]	29.00	29.00
Heat Flow [kJ/min]	-12.99	-28.02

Table-11. Molar flow rates of the components around the conversion reactor top product condenser.

Component	gmol/min	
	Input	Output
Methanol	0.0081	0.0081
Dimethyl ether	0.0169	0.0169
Water	0.1132	0.1132
Ethylene	0.3478	0.3478

The results given in Table-11 were for the material flow around the condenser. As there was no material exchange around the condenser, the amount of each component entering was the same as the amount leaving the condenser.

3.6 Balances around conversion reactor products mixer

The product coming out of the bottom of the conversion reactor and that leaving the conversion reactor condenser were also mixed before passing the mixture further for separation, and the results obtained from the mixing carried out are given in Table-12. From the results

in Table-12, it was noticed that about 0.32 fraction of the mixed liquid was vapourized in the mixer. This was due to the fact the temperature difference between the two liquid streams being mixed was much, and it was desired to mix

the streams at atmospheric pressure. Hence, there was vapourization to some extent. Despite that, the heat load around the mixer was estimated to be 0 kJ/min.

Table-12. Operating conditions and energy flow of the conversion reactor mixer.

Name	Top Input	Bottom Input	Output
Vapour Fraction	0.00	0.00	0.32
Temperature [^{o}C]	-123.49	63.90	-70.39
Pressure [atm]	1.00	1.00	1.00
Molar Flow [gmol/min]	0.49	0.61	1.09
Mass Flow [g/min]	12.84	11.03	23.87
Liquid Volume Flow [mL/min]	29.00	11.13	40.12
Heat Flow [kJ/min]	-28.02	-170.75	-198.77

Table-13. Molar flow rates of the components around the conversion reactor products mixer.

	gmol/min		
Component	Top Input	Bottom Input	Output
Methanol	0.0081	0.0046	0.0127
Dimethyl ether	0.0169	0.0014	0.0183
Water	0.1132	0.6008	0.7140
Ethylene	0.3478	0.0000	0.3478

The molar flow rates of the components involved in the mixing operation of the process are given in Table-13. Owing to the fact that there was not any reaction occurring in the mixer, the total amount of each

component entering the mixer was equal to the amount of the component in the mixed output stream. For a mixer working properly, this was, actually, supposed to be so.

3.7 Balances around separation column
In order to obtain high purity of the desired product, which was ethylene, the mixed liquid was passed into a separation column, and the results given from the simulation of the process with the separation were as shown in Table-14 for the operating conditions of the separation and its energy flow. According to the results, the top output of the separation was observed to be pure vapour while the material leaving the bottom section was pure liquid because the vapour fractions were 1 and 0, respectively.

Table-14. Operating conditions and energy flow of the separation column.

Name	Input	Top output	Bottom output
Vapour Fraction	0.32	1.00	0.00
Temperature [^{o}C]	-70.39	-70.39	-70.39
Pressure [atm]	1.00	1.00	1.00
Molar Flow [gmol/min]	1.09	0.35	0.75
Mass Flow [g/min]	23.87	9.75	14.12
Liquid Volume Flow [mL/min]	40.12	25.41	14.71
Heat Flow [kJ/min]	-198.77	16.67	-215.44

Table 15. Molar flow rates of the components around the separation column.

	gmol/min		
Component	Input	Top output	Bottom output
Methanol	0.0127	0.0000	0.0127
Dimethyl ether	0.0183	0.0006	0.0177
Water	0.7140	0.0000	0.7140
Ethylene	0.3478	0.3465	0.0014

The material flow, in terms of molar flow rates, around the separator was also considered, and the results of this consideration are given in Table-15. The results obtained for the separator were also found to be supporting the validity of the developed Aspen HYSYS model of the methanol-to-olefin process for design because the total molar flow rate of each of the components in the output streams was the same as the molar flow rate of each of them in the input stream. It was noticed from the results given in Table-15 that ethylene had a very high mole fraction in the top output of the separator. In other words,

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the desired product was obtained from the top section of the separation column. As such, the vapour leaving the top section of the separator was condensed in order to obtain the desired product in liquid form.

3.8 Balances around separation column top product condenser

The results obtained from the condensation operation of the top product of the separator, which was the desired product of the process, are given in Table-16. As usual with condensers, the vapour fractions of the input and the output were found to be 1 and 0 respectively, indicating that total vapour entered the condenser while total liquid exit it as the product at atmospheric pressure.

Table-16. Operating conditions and energy flow of the separation column top product condenser.

Name	Input	Output
Vapour Fraction	1.00	0.00
Temperature [^{o}C]	-70.39	-116.80
Pressure [atm]	1.00	1.00
Molar Flow [gmol/min]	0.35	0.35
Mass Flow [g/min]	9.75	9.75
Liquid Volume Flow [mL/min]	25.41	25.41
Heat Flow [kJ/min]	16.67	11.23

It was also discovered from the results that the amount of each component that entered the condenser was the same amount of each of them leaving it (the condenser), as given in Table-17, as the condenser was only meant to change the phase of the material and not for any material transfer.

Table-17. Molar flow rates of the components around the separation column top product condenser.

Component	gmol/min		Mole fraction
	Input	Output	
Methanol	0.0000	0.0000	0.0000
Dimethyl ether	0.0006	0.0006	0.0019
Water	0.0000	0.0000	0.0000
Ethylene	0.3465	0.3465	0.9981

In order to know whether the product is of high purity, the mole fractions of the components leaving the separator top product condenser were determined, and the results are given in Table-17. According to the information obtained from the mole fraction results given in the table, the desired product was observed to have been obtained at very high purity because its mole fraction was obtained to be very close to 1 (see Table-17).

4. CONCLUSIONS

The simulation of the model developed for the design of a methanol-to-olefin process carried out with the aid of Aspen HYSYS showed that the model was a valid one because the results were found to be in agreement with the principles involved in the pieces of process equipment used. Moreover, it was discovered from the design that the material flow around each of the pieces of the process equipment given by Aspen HYSYS were balanced because, where there was neither consumption nor generation, the total amount of input for each component was equal to that of the output. Furthermore, the energy balances revealed that the all the process equipment involved were having heat duties of 0 kJ/min except the condensers.

NOMENCLATURE

EquilReactor	Equilibrium reactor
ConvReactor	Conversion reactor
NRTL	Non-Random Two-Liquid
ERTopCondenser	Equilibrium reactor top product condenser
ERMixer	Equilibrium reactor products mixer
CRTopCondenser	Conversion reactor top product condenser
CRMixer	Conversion reactor products mixer
SCTopCondenser	Separation column top product condenser

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