Simulation Studies of Selective Methylation of Toluene using UniSim and Spreadsheet Interface

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P-xylene is a colorless, highly flammable, toxic, transparent chemical. Stable demand from polyester manufacturers emerged as one of the major driving factors for the production of P-xylene. There are various methods reported for manufacturing p-xylene. The catalytic reforming of naphtha, toluene disproportionation, and methylation of toluene are some of the methods used for P-xylene production. The objective of this project was to develop a steady-state process flow diagram for the continuous production of p-xylene using UniSim design software. Complete design of the distillation column and plug flow reactor with optimum values from the UniSim design suite is reported. In this process, methanol and toluene at a particular temperature and pressure are mixed and fed to the plug flow reactor, and the product stream from the plug flow reactor is separated based on their phases and distilled to obtain pure p-xylene and methanol is recycled. A detailed design with materials and energy balance using a spreadsheet interface are presented in the paper. This optimization promotes reducing the production of other isomers of xylene, resulting in a reduction of separation cost.

Keywords: Steady-state, Plug Flow Reactor, Separators, Optimization, Property model, Spreadsheet.

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1. Introduction

Xylene is an aromatic hydrocarbon having two methyl groups attached to the benzene ring. There are three isomers named ortho-xylene, meta-xylene, and para-xylene. Para- xylene is an isomer where the methyl group is attached at the para position.It is a colorless, highly flammable, toxic, transparent chemical.The growing demand for plastic is the ultimate reason for the rise in demand for p-xylene used in the manufacture of polyethylene terephthalate (PET)[1].The annual capacity of para-xylene was estimated to be around 26 billion tones. Due to a growth in the usage of PET in plastic bottles, the global use of para-xylene is expected to expand at a pace of 7% per year over the next five years [2]. Asia's growth is predicted to be even faster, at an annual rate of 8.5 percent. The utilization rate of para-xylene is predicted to remain steady at around 90% of global capacity over the next five years; nevertheless, due to a 6% annual increase in global PET bottle production capacity, para- xylene's current production capacity is far from adequate [2-3].There are various methods to produce p-xylene, but industrially most p-xylene is produced by majorly two methods. The first method is the catalytic reforming of naphtha, and the second method is the methylation of toluene. Catalytic reforming of naphtha requires the separation of mixtures that include benzene, toluene, and xylene. The cost of separation increases the overall cost of the entire process and thus preferred the least [4-5].Since the process of methylation can be enhanced using specific deftness, a methylation reaction is preferred[1].

2. Methodology

Methylation of the toluene process was selected as its more economical than the catalytic reforming of naphtha. A ProcessFlow Diagram (PFD) of the proposed process to produce p-xylene was developed using UniSim software with Non-Random Two-Liquid (NRTL) property model [5]. The strategy for making the base case is to model the steady state operation of the process. Further the process variables of reactor are optimized using UniSim simulation tool to get high p-xylene selectivity [6-7].

2.1 Development of PFD

Toluene and methanol are fed at a temperature of 25°C and a pressure of 1 bar. The reaction will occur in the gas phase at a temperature of 400°C and pressure of 3 bars. Before entering the reactor, we need to increase both temperature and pressure from atmospheric conditions to reactor conditions. Methanol and toluene were fed to two different centrifugal pumps respectively, to increase the pressure. The compressed solutions are passed into the respective heater to increase the temperature. These two solutions were made to mix in a mixer after which it enters the Plug Flow Reactor (PFR). The product stream from PFR is flashed into Vapor Liquid Separator (VLS) where differential separation occurs between vapor and liquid streams.The bottom stream of VLS is fed to DC-1 (T-100) where distillate is a mixture of methanol and water which is further passed to DC-3(T-102) and the residue is p-xylene. The top stream of VLS is fed to DC-2(T-101) where distillate is a mixture of methanol and water which is further passed to DC-3 and residue is p-xylene. In DC-3 distillation of methanol and water mixture occurs. The distillate stream is pure methanol which was recycled back to complete the closed-loop of the flow diagram as depicted in Figure 1.
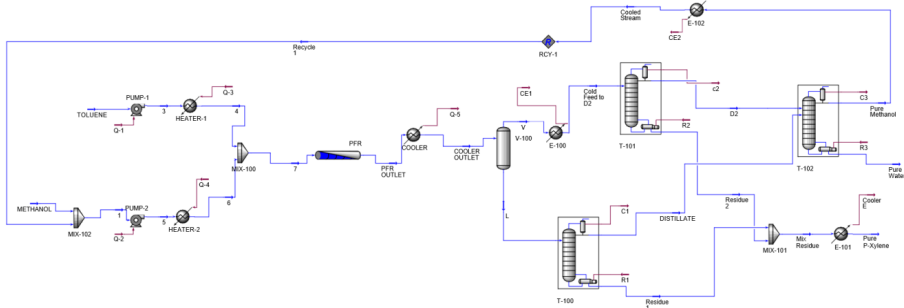
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Fig. 1. Complete process flow diagram for p-xylene production

Table1. Pump and Heater conditions

	Methanol		Toluene	
	IN	OUT	IN	OUT
Pump	100kPa	300kPa	100kPa	300kPa
Heater	25°C	400°C	25°C	400°C

Table2. Feed condition to the PFR reactor

Name	Toulene	Methonal	Feed to PFR
Vapour	1.0000	1.0000	1.0000
Temperature [C]	400.2	400.1	400.1
Pressure [kPa]	300.0	300.0	300.0
Molar Flow [kgmole/h]	190.0	1201	1391
Mass Flow [kg/h]	1.751e+004	3.847e+004	5.598e+004
Std Ideal Liq Vol Flow [m3/h]	20.12	48.34	68.46
Molar Enthalpy [kJ/kgmole]	1.111e+005	-1.795e+005	-1.398e+005
Molar Entropy [kJ/kgmole-C]	145.9	211.6	205.9
Heat Flow [kJ/h]	2.110e+007	-2.155e+008	-1.944e+008

Table 1 shows the pump and heater inlet and outlet conditions applied for the steady simulation using UniSim simulation tool. Table 2 illustrates the feed conditions applied for the plug flow reactor. The heat flow condition, molar flow rate, temperature and pressure conditions in the reactor and the inlet streams of the reactors are shown in detail. The conditions are such that the reactor is operated isothermally. The temperature of the plug flow reactor was maintained at 400.1 ℃.

2.2 Design procedure of Distillation column

Equilibrium Data for the binary system was derived from UniSim simulation results. The McCabe-Thile procedure was adopted to estimate the number of stages required for the separations[8-9]. The Equilibrium curve was drawn using the equilibrium data. The Feed conditions and the desired separation achieved from the simulation results are markedon the equilibrium curve. The spread sheet

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was programmed so that the once the initial feed, distillate and residue composition are feed the McCabe-Thile plot is plotted.

The operating line equation shown in Eq 1 for rectifying section was considered to estimating the slope and intercept of the operating line.

$$Y = \frac{R \cdot Xn}{(R+1)} + \frac{Xd}{(R+1)} \dots \dots \dots \dots \dots . (1)$$

The feed line shown in Eq 2 was considered; slope of the line was estimated and feed into the spread sheet to cut the rectifying section operating line.

$$Y = \frac{q \cdot X}{(q-1)} + \frac{Xf}{(q-1)} \dots \dots \dots \dots \dots \dots \dots . (2)$$

The intersection point from operating lines of rectifying and feed line section is joined with (X_w, X_w). Drawing triangles between the equilibrium curve and the operating lines of the three sections. The number of triangles drawn is equal to the number of ideal trays.The height of the distillation column was calculated using the Eq 3,

Height of the column = {(No. of trays − 1)*Distance between each ray} + Top chamber height + Bottom chamber height   .... (3)

2.3 Design procedure of Plug Flow Reactor

$$\text{Conversion} = \frac{\text{Stoichiometry Coefficient} * \text{Reaction Coordinate}}{\textit{Number of moles of Toluene}} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (4)$$

Based on the initial concentration of methanol and toluene it was observed that this reaction was pseudo first order reaction. Using Arrhenius's theory, the rate constant of the reaction was determined and subsequently the rate of reaction. Using the design equation Eq 5 of plug flow reactor volume of the reactor was calculated [10-12].

$$\int_0^{X_a} \frac{dX_a}{-r_A} = \frac{V}{F_{A0}} \dots \dots \dots \dots \dots (5)$$

The reaction is first order in nature, therefore for first order and at constant temperature the Equation 5 reduces to different form as shown in Eq 6.

$$\frac{V}{F_{A0}} = \left(\frac{1}{K \times CA_0}\right) \times \int_0^{X_a} \frac{dX_a}{1 - X_a} \dots \dots \dots \dots \dots \dots \dots \dots (6)$$

3. Results and Discussions

The paper discusses majorly on the design of the binary component distillation column using a programmed spread sheet and the design of the plug flow reactor considering the effect of reactor length and diameter. The distillation column was optimized in a stage-wise manner. The temperature change in each tray was analyzed and number of stages were optimized without any change in the condenser load, reboiler load and composition of the distillate. All the three distillation operations in the process were optimized by same procedure. The design of the plug flow reactor using actual calculation was verified with the help of volume considered from the obtained data in the simulation software. It was compared with the performance equation which was theoretically calculated. The result obtained with the help of the performance equation, given in section 2.3, was approximately

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equal to the value of the volume in the UniSim software. The above design was thus found to be in line with the aim of the work.

3.1 Design of Binary Component Distillation Column

Overall material balance was analytically verified with obtained UniSim results for all three distillation columns. The height of all three columns was calculated considering the spacing between the trays, top and bottom chamber height. The design of the column T-102 (D3) was done using the McCabe Thiele method using a spreadsheet interface. The T-102 distillation column is a binary component distillation column; hence a spread sheet was programed for plotting the number stages in the column using the principle of McCabe Thiele method [13].

The results Input data applied in the spread sheet is shown in Table 3. The Table 4depicts the composition of feed, distillate and residue streams obtained from the UniSim simulation for all the distillation columns. These composition data are applied further in spread sheet to trace the McCabe Thiele method to estimate the number stages repaired to methanol- water separation in the T-102 (D3) column. The results obtained from the spread sheet is shown in Figure 2 and Table 5. Figure 2, is the Mecabe Thiele plot for the binary separation of methanol-water system.

Table 3. Input value of distillation column

Relative Volatility	α	6
Mole Fraction in Feed	X_F	0.84
Mole Fraction in Distillate	X_D	0.999
Mole Fraction in Bottom	X_B	0
Quality of Feed	q	1
Minimum Reflux Ratio	R_{min}	0.23
Reflux Ratio	R	2

Table 4. Composition of distillation column

	Feed				Distillate				Residue			
	Methanol	Water	Toluene	p-xylene	Methanol	Water	Toluene	p-xylene	Methanol	Water	Toluene	p-xylene
DC-1	0.5357	0.2204	0	0.2438	0.7085	0.2914	0	0.000002	0	0.0001	0	0.9999
DC-2	0.8683	0.0752	0	0.0564	0.9202	0.0797	0	0.000003	0	0.0001	0	0.9999
DC-3	(i)0.7085	0.2914	0	0.000002	0.999	0.000999	0	0	0	0.99998	0	0.000013
	(ii)0.9202	0.0797	0	0.000003								

Table 5. Number of stages as computed using spread sheet

Stages	X	Y	Stages	X	Y
1	0.999	0.999	7	0.086	0.091
	0.994	0.999		0.016	0.091
2	0.994	0.996	8	0.016	0.017
	0.975	0.996		0.003	0.017
3	0.975	0.983	9	0.003	0.003

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	0.905	0.983		0.001	0.003
4	0.905	0.936	10	0.001	0.001
	0.710	0.936		0.000	0.001
5	0.710	0.755	11	0.000	0.000
	0.339	0.755		0.000	0.000
6	0.339	0.360	12	0.000	0.000
	0.086	0.360			

The number stages obtained from the programmed spread sheet are shown in Table5. Table 5depicts that the number stages required are 13 including reboiler for the operation according to the McCabe Thiele method. Considering the efficiency of each stage to be around 50% the total number of stages required are 26, This is equal to the optimized value obtained in the UniSim simulation for T102 (D3) column as shown in Table 6.
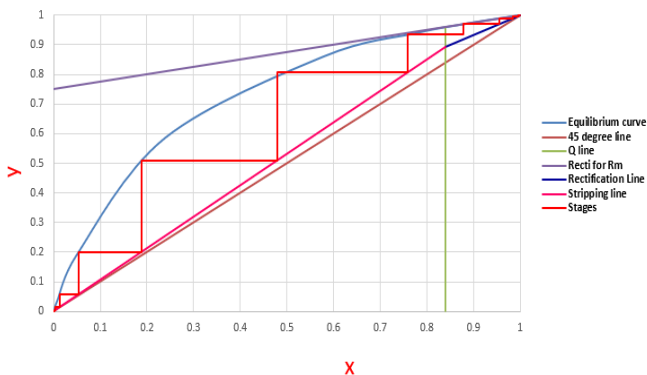
Fig. 2. McCabe–Thiele curve from the spread sheet

3.2 Optimization of Number Stages Distillation Column

From Figure 3. the number of stages in a steady state of distillation column T-100 (D1) was 50. On studying the temperature versus tray position graph, it was observed that at a particular same temperature range multiple tray compositions were found out to be equivalent [14]. Hence the optimization tool in the Unisim simulation design suit was used to estimate the optimum number of trays required without change in the final purity of components in distillate and residue stream. Finally, the number of trays was optimized to 20.
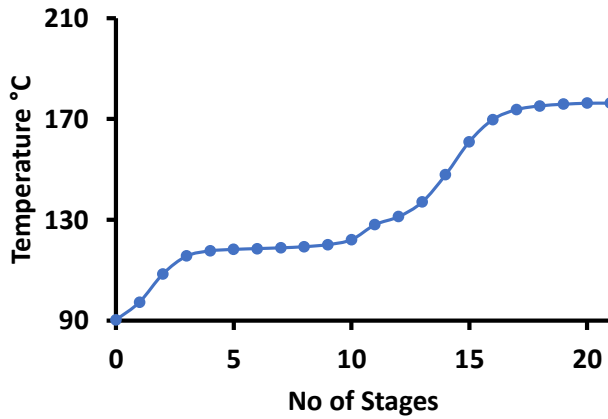
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Fig. 3. Temperature vs. Tray Position of DC-1
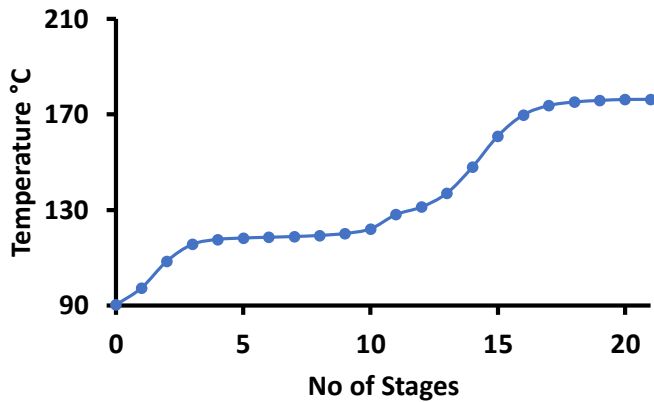

Fig. 4. Temperature vs. Tray Position of DC2

From Figure4 the number of stages in a steady state of distillation column T-101 (D2) was 30. On studying the temperature versus tray position graph, it was showed similar behaviour as in D1 column resulting in multiple tray compositionswere found out to be equivalent for the same temperature range. Hence the optimization tool in the Unisim simulation design suit was used for D2 column to estimate the optimum number of trays required without change in the final purity of components in distillate and residue stream.Therefore, the number of trays was optimized to 18.
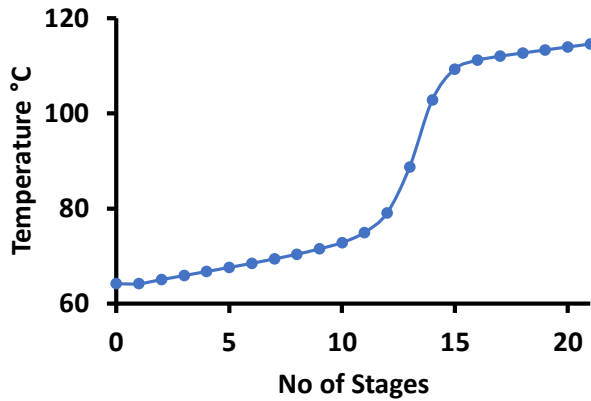
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Fig. 5. Temperature vs. Tray Position of DC3

From Figure5 the number of stages in a steady state of distillation column T-102 was 40. Temperature versus tray position graph, it was observed that at a particular same temperature range multiple tray compositions were found out to beequivalent.Hence the optimization tool in the Unisim simulation design suit was used for D2 column to estimate the optimum number of trays required without change in the final purity of components in distillate and residue stream. Therefore, the number of trays was optimized to 25.

Table 6. Optimised characteristics of distillation column

Distillation Column	Number of Stages	Feed Stage Location	Molar Reflux Ratio	Distillate Rate, Kmol/hr	Reboiler Pressure kPa	p-Xylene Product Purity
DC – 1	20	10	3.5	449.8	250	0.999
DC – 2	18	9	6	751.1	220	0.999
DC – 3	25	12	2	1011	180	0.999

From Figure6 it can be inferred that by optimizing the distillation columns the number of traysis significantly reduced and thus reduces the cost and the area occupied. The optimized trays are not affecting the purity of the end product. The condenser load and reboiler load calculations were considered during optimization and the energy require for both condenser and reboiler was kept in a balanced state.

3.3 Plug Flow Reactor Calculations

Using the conversion equation, the result obtained is 100% i.e.,

$$\frac{(|-1| * 190)}{(1391 * 0.14)} = 1$$

The molar Concentration Ratio is 6.142

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Since the value of m is very high, the above reaction is considered a pseudo-first-order reaction. A pseudo-first-order reaction is said to be a second-order reaction or bimolecular reaction that is made to behave like a first-order reaction [15].
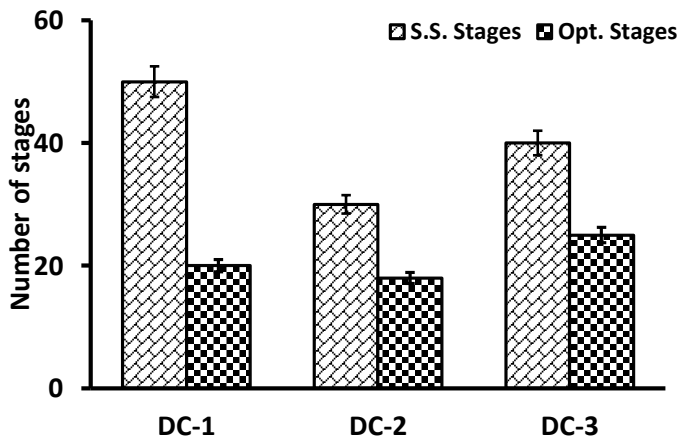

Fig. 6. Comparison plot for steady-state operation and optimized operation

Rate Constant is given by rate = K $[A]^1$

where K = 495 s^{-1}

The concentration and Molar flow rate of the A component is 7.506 mol/m^3 and189.89 kmol/hr respectively. The volume of the reactor is 0.067 m^3

4.Conclusion

Methylation of toluene produces p-xylene and the result of high p-xylene selectivity at low contact time withthe UniSim optimization tool is used to maximize the purity of p-xylene by optimizing the reactor and distillation column parameters. The product of the process is 99.9% p-xylene with an overall 100% conversion of feed toluene to xylene. Due to the increase in demand for p-xylene, this process can be used to produce p-xylene efficiently. The major area for optimizing the process is the number of stages in the distillation columns and this is done using UniSim software. The best-optimized flow diagram decreases the number of stages nearly to half of the stages used in a steady-state. Required material and energy balance was achieved. The volume of the plug flow reactor was calculated analytically and was equivalent tothe UniSim result. The height of the distillation column and the number of trays were calculated.

Acknowledgement

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