

Process of *p*-Xylene Production by Highly Selective Methylation of Toluene[†]

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ABSTRACT: *p*-Xylene is an important industrial compound, and its demand has been increasing in recent years. It is mostly produced from cracking of naphtha, but there is a need for new and cost-effective methods for the production. Toluene alkylation with methanol over an aluminosilicate zeolite catalyst, such as ZSM-5, produces a mixture of xylene isomers with low *p*-xylene selectivity. Due to the very close boiling points of xylene isomers, it is very expensive to separate them. There has been some success in enhancing *p*-xylene selectivity by modifying the ZSM-5 catalyst. This results in reduced separation cost, which makes toluene methylation a competitive process for *p*-xylene production. Based on these findings, a novel process for the production of *p*-xylenes by the catalytic methylation of toluene followed by reactive distillation for the separation of *p*-xylene (instead of the more costly conventional technique of separation based on crystallization and adsorption) is developed and a complete process flow diagram is simulated using Aspen Plus. Using the built-in optimization tool in Aspen Plus, we optimized reactor parameters for a maximum *p*-xylene selectivity of 97.7%. After separation, a *p*-xylene product stream purity of 99.7% is achieved. High *p*-xylene selectivity in the reactor and use of reactive distillation reduces the separation cost and renders the new process economically competitive.

1. INTRODUCTION

p-Xylene is one of the three xylene isomers with a methyl group attached to the para position of the benzene ring. It is industrially more important than the other isomers, *m*-xylene and *o*-xylene, due to its use for the production of terephthalic acid that is used for the production of polyethylene terephthalate (PET); PET is used to produce polyester fiber and films, and PET bottles.¹ Due to its high downstream applications, *p*-xylene generally has 6–8% annual demand growth.² Most *p*-xylene comes from catalytic re-forming of naphtha.³ Xylene isomers, along with other aromatics such as benzene and toluene, are produced from catalytic re-forming of naphtha. Conventionally, after separation of aromatics, *p*-xylene is separated from the other xylene isomers by crystallization or adsorption.⁴ Due to the very close boiling points of the different xylene isomers (Table 1), separation of

also produces benzene; therefore, it is feasible when benzene is also required along with the xylenes.⁷ Methylation of toluene is carried out with methanol over a zeolite catalyst, which produces water and xylenes. The production is feasible if the cost of methanol is low and the selectivity of *p*-xylene is high.⁸

The reaction of toluene and methanol over a zeolite catalyst, such as ZSM-5, yields water and xylenes with the following thermodynamic equilibrium composition of xylene isomers: 23.55% *p*-xylene, 52.42% *m*-xylene, and 24.03% *o*-xylene at 400 °C.⁹ Due to very close boiling points of xylene isomers it is usually not easy to separate *p*-xylene. Also, other isomers do not have much industrial demand and isomerization is needed to convert them to *p*-xylene.⁴ Methylation of toluene is a suitable option if *p*-xylene can be produced with high selectivity. Different modifications of zeolite catalysts has resulted in high *p*-xylene selectivity.^{10–13} The higher *p*-xylene selectivity over the modified zeolite, used in Faramawy,¹⁴ is attributed to the removal of external surface acid sites and smaller pore openings size.¹⁴ Methylation of toluene, in addition to some other side reactions such as xylene isomerization, occurs inside the pores of the zeolite catalyst. Mirth et al.¹⁵ have reported that diffusion plays an important role in the transport of xylenes from the pores' inside out, and that the diffusion coefficient of *p*-xylene can be about 100 times that of *o*-xylene and about 1000 times that of *m*-xylene above 250 °C. Due to high *p*-xylene diffusivity, the concentrations of *m*-xylene and *o*-xylene increase inside the pores, thus promoting their isomerization to *p*-xylene and enhancing *p*-xylene selectivity.¹⁶ Isomerization of *p*-xylene also occurs on zeolite external sites, which reduces *p*-xylene selectivity.¹⁷ The *p*-xylene selectivity can

Table 1. Boiling and Freezing Points of Xylene Isomers²⁶

isomer	normal boiling point, °C	freezing point, °C
<i>p</i> -xylene	138.3	13.3
<i>m</i> -xylene	139.1	−47.85
<i>o</i> -xylene	144.4	−25.16

p-xylene from xylene mixtures is difficult and represents an extensive energy step in the whole production process. Due to increasing demand, there is a need for new and cost-effective processes for the production of *p*-xylene. Other methods for the production of *p*-xylene include toluene disproportionation and toluene methylation. Toluene has the lowest demand as compared to that for benzene and xylenes, and there is a strong incentive to convert surplus toluene to more valuable aromatics.⁴ In toluene disproportionation, two molecules of toluene react over an acid zeolite catalyst to form one xylene and one benzene molecule.⁵ In toluene disproportionation, a *p*-xylene selectivity of 90%, from total xylenes produced, is achievable.⁶ This process

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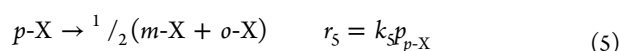
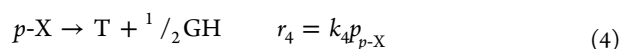
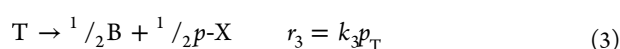
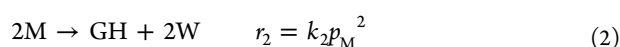
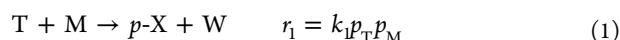
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be increased by zeolite modification, which neutralizes the unselective external acid sites and also reduces the effective catalyst pore size.¹⁸ High space velocity (equivalent to low space time) reduces the contact time at the external surface and suppresses the xylene isomerization reaction over the external surface.⁸ Breen et al.⁸ have reported *p*-xylene selectivity close to 100% by using Mg modified ZSM-5 catalyst at low space time. Sotelo et al.¹⁹ have also reported that *p*-xylene selectivity approaches 100% as space time tends to zero over Mg modified ZSM-5 catalyst; this is attributed to diffusional resistance to other isomers. High *p*-xylene selectivity results in negligible production of unwanted xylene isomers and significant reduction in the separation cost of *p*-xylene.

To increase *p*-xylene production, the direct conversion of toluene to *p*-xylene is a desirable alternative. This work integrates toluene methylation and separation of *p*-xylene, to provide a complete process to produce *p*-xylene with the required purity. The novel process does not require classical xylene separation technologies such as crystallization or adsorption. Instead, *p*-xylene is purified by reactive distillation to meet the product purity specification. Aspen Plus process simulator is used to simulate the proposed process, which utilizes catalytic methylation of toluene over Mg-modified ZSM-5 zeolite catalyst.

2. KINETIC MODEL

Kinetic data for toluene methylation over Mg-modified ZSM-5 catalyst is reported by Valverde.²⁰ The catalyst used contains 1.09 wt % Mg, has 35 wt % sodium montmorillonite as a binder, and has an average particle size of 0.75 mm. The five reactions involved, together with their intrinsic and observed rate expressions,²⁰ are given in eqs 1–5. The reactions considered are (1) toluene methylation, (2) methanol dehydration, (3) toluene disproportionation, (4) *p*-xylene dealkylation, and (5) *p*-xylene isomerization, respectively.



In the above equations, k denotes rate constant and p represents partial pressure. Gaseous hydrocarbons (GH) represent light species (e.g., methane, ethane, ethylene, propane, propene, and butanes) that are produced during methanol dehydration and *p*-xylene dealkylation reactions. GH is used to collectively represent gaseous hydrocarbons in the kinetic study by Valverde.²⁰ In this study, GH is modeled as pure ethylene as it balances the stoichiometric equations. In the *p*-xylene isomerization reaction, eq 5, equal amounts of *m*-xylene and *o*-xylene are assumed to be formed as in Sotelo et al.¹⁹ The reactions given in eqs 1, 3, and 4 occur inside the pores of the catalyst, and the effectiveness factors η_1 , η_3 , and η_4 are used to account for diffusion limitations.²⁰ The kinetic model parameters²⁰ are given in Table 2, whereas the values of the effectiveness factors, η_3 and η_4 are given in Table 3 for three different temperatures: 460, 500, and 540 °C. The value of effectiveness factor η_1 is 0.98²⁰ and can be considered as equal to 1 as a good approximation.

Table 2. Kinetics of Toluene Methylation over Mg Modified ZSM-5 Catalyst²⁰

parameter	pre-exponential factor, A_p , mol/(g·h·atm ²) or mol/(g·h·atm)	activation energy, E_p , kJ/mol
k_1	403 ± 5	45.7 ± 0.4
k_2	1346 ± 64	50.6 ± 0.5
k_3	96.2 ± 1	59.0 ± 0.5
k_4	0.3815 ± 0.05	19.6 ± 0.7
k_5	46.94 ± 0.5	48.9 ± 0.3

Table 3. Effectiveness Factors for Toluene Methylation over Mg Modified ZSM-5 Catalyst²⁰

temp, °C	η_3	η_4
460	0.7781 ± 0.117	2.977 ± 1.10
500	0.5355 ± 0.170	3.212 ± 0.59
540	0.4470 ± 0.320	3.201 ± 0.97

Using the kinetic parameters and model of Valverde,²⁰ an isothermal packed bed reactor is simulated using Aspen Plus. The simulation results are compared in Figures 1 and 2 with the experimental data reported in Figures 6 and 7 in Sotelo et al.¹⁹ The simulation results are found in good agreement with the experimental data.¹⁹ The effects of temperature, pressure, space time (weight of catalyst per unit feed flow rate of toluene, W_{cat}/F_{T_0}), and toluene-to-methanol feed ratio, F_{T_0}/F_{M_0} , on toluene conversion, xylene selectivity, and *p*-xylene selectivity are analyzed using the sensitivity analysis feature in Aspen Plus. Conversion, C , is defined as the percentage of toluene reacted, total xylenes selectivity, S_x , is the percentage of toluene reacted to form xylenes, and *p*-xylene selectivity, S_p , is the percentage of *p*-xylene from total xylenes formed.

Figure 3 shows the effect of temperature on conversion C and selectivities S_x and S_p . As the temperature increases, there is an increase in toluene conversion but xylene selectivity drops and a more significant decline in *p*-xylene selectivity is noticed. This means that side reactions become more important as the temperature increases; therefore, high *p*-xylene selectivity is favored at low temperature. Figure 4 shows the effect of pressure on C , S_x , and S_p . With an increase in pressure toluene conversion increases, but there is a drastic drop in *p*-xylene selectivity; thus, low pressure in the reactor is required to achieve high *p*-xylene selectivity. The effects of space time on C , S_x , and S_p are studied. At low values of space time, there is high *p*-xylene selectivity but with low conversion, which is consistent with the experimental results reported in Figure 4 in Sotelo et al.¹⁹ The low space time means low contact time at the surface of the catalyst which lessens the unwanted isomerization of *p*-xylene to *m*-xylene and *o*-xylene.⁸ Low space time can be achieved with high toluene feed rate. The effect of toluene-to-methanol feed ratio is also studied, and the results are in agreement with the experimental results reported in Figure 5 in Sotelo et al.¹⁹ With an increase in feed ratio, there is not much of a change in selectivity, but there is a decrease in toluene conversion. This result is in agreement with the experimental results in Figure 5 in Sotelo et al.¹⁹ Low toluene-to-methanol feed ratio results in more methanol loss due to methanol dehydration reaction. It is worth mentioning that at a toluene-to-methanol feed ratio of 1, a temperature of 500 °C, and $W_{\text{cat}}/F_{T_0} = 15$ (g h)/mol, about 82% of the reacted methanol is consumed by side reactions.

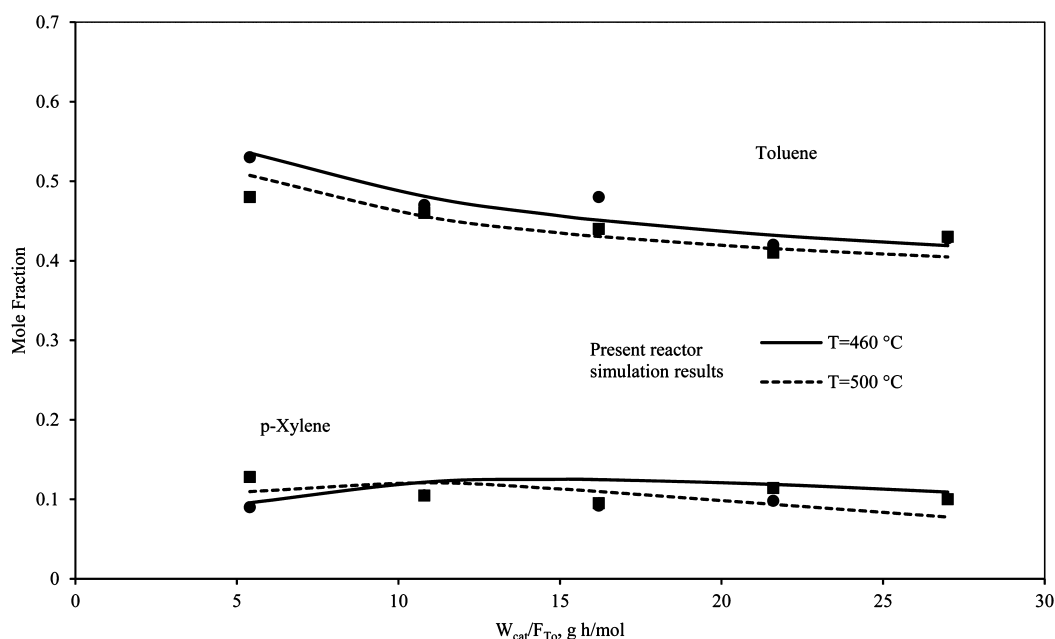


Figure 1. Comparison between experimental data reported in Figure 6 in Sotelo et al.¹⁹ (●, 460 °C; ■, 500 °C) and present reactor simulation results ($F_{T0}/F_{M0} = 2$).

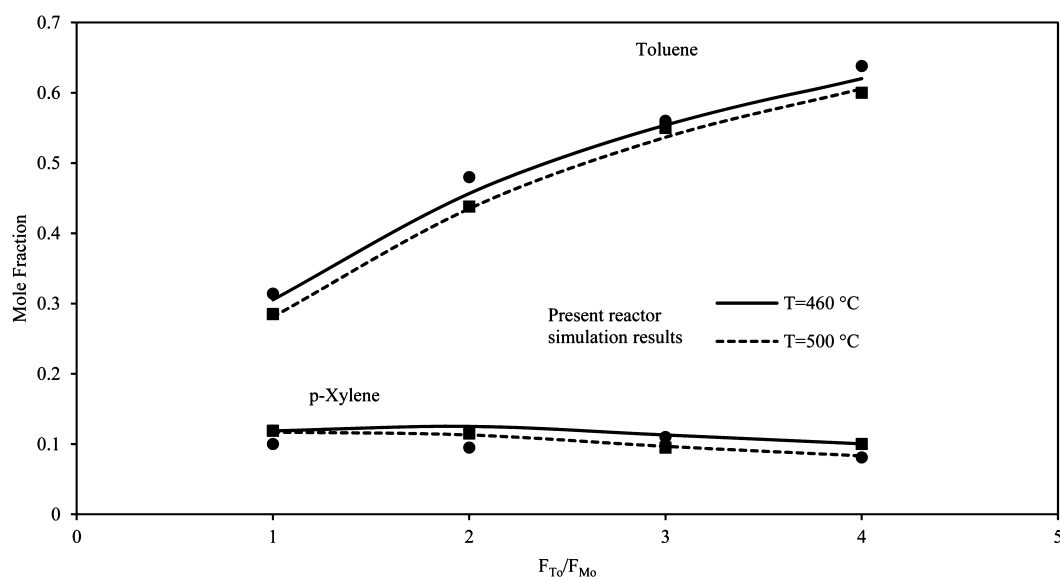


Figure 2. Comparison between experimental data reported in Figure 7 in Sotelo et al.¹⁹ (●, 460 °C; ■, 500 °C) and present reactor simulation results ($W_{cat}/F_{T0} = 15$ (g h)/mol).

3. REACTOR MODELING AND OPTIMIZATION

The parameters affecting the toluene methylation reactor are adjusted so that the process is operable and high *p*-xylene selectivity is achieved. Sensitivity analysis shows that high *p*-xylene selectivity is favored at low temperature, low pressure, and low contact time. Although low pressure is advantageous, a pressure of 3 bar is selected to account for the pressure drop in the reactor and downstream heat exchangers. Typically the pressure drop in packed bed is less than 10% of the inlet pressure²¹ and the pressure drop in heat exchangers is in the range 0.1–0.5 bar.²² Pressure higher than 3 bar lowers the *p*-xylene selectivity as shown in Figure 4. Aspen Plus optimization tool²¹ is used to optimize the values of temperature, toluene-to-methanol feed ratio, and space time in the reactor. The sequential quadratic programming (SQP) algorithm is selected to solve the

optimization problem. The objective function, given by eq 6, is maximum *p*-xylene selectivity. It is defined in the optimization tool input form using a Fortran statement. The toluene feed flow rate is set to 1000 kmol/h while values of catalyst loading, W_{cat} , and methanol feed flow rate, F_{M0} , are used as adjustable variables for optimizing values of space time, W_{cat}/F_{T0} , and methanol-to-toluene feed ratio, F_{T0}/F_{M0} . A methanol loss to side reactions of 40% is used as a constraint; it is calculated as shown in eq 7 and input in the optimization tool as a Fortran statement. Table 4 shows the starting values and the results of Aspen Plus optimization tool. The *p*-xylene selectivity is increased from 58.0% to 97.7% by optimizing the reactor inlet temperature, toluene-to-methanol feed ratio, and space time; the optimum values are found to be 400 °C, 2, and 2.5 (g h)/mol, respectively. Furthermore, methanol loss to side reaction is decreased

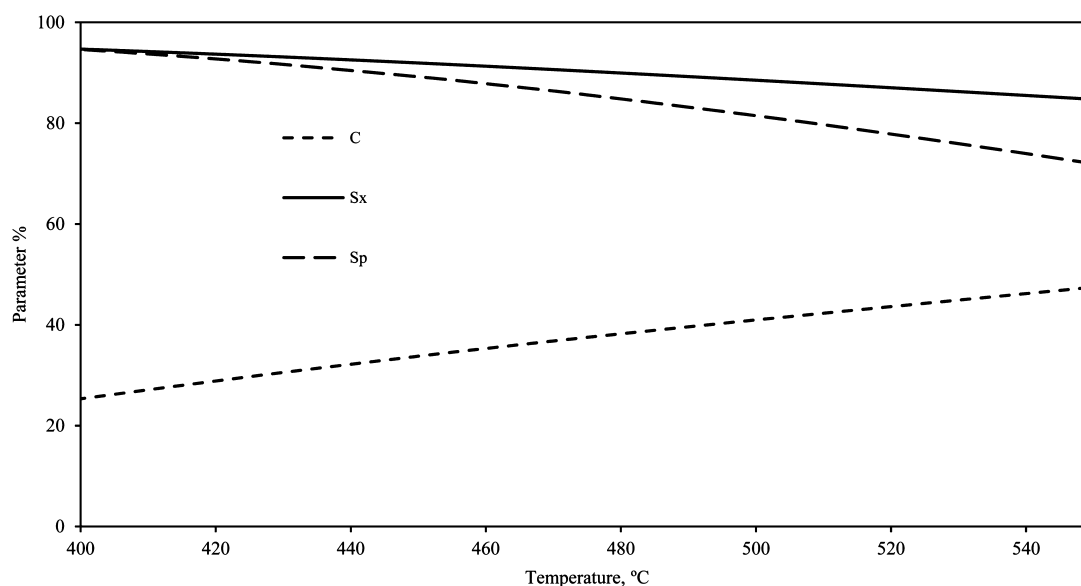


Figure 3. Effect of temperature on conversion, total xylenes selectivity, and *p*-xylene selectivity ($F_{T0}/F_{M0} = 1$, $W_{cat.}/F_{T0} = 15$ (g h)/mol, pressure = 1 bar).

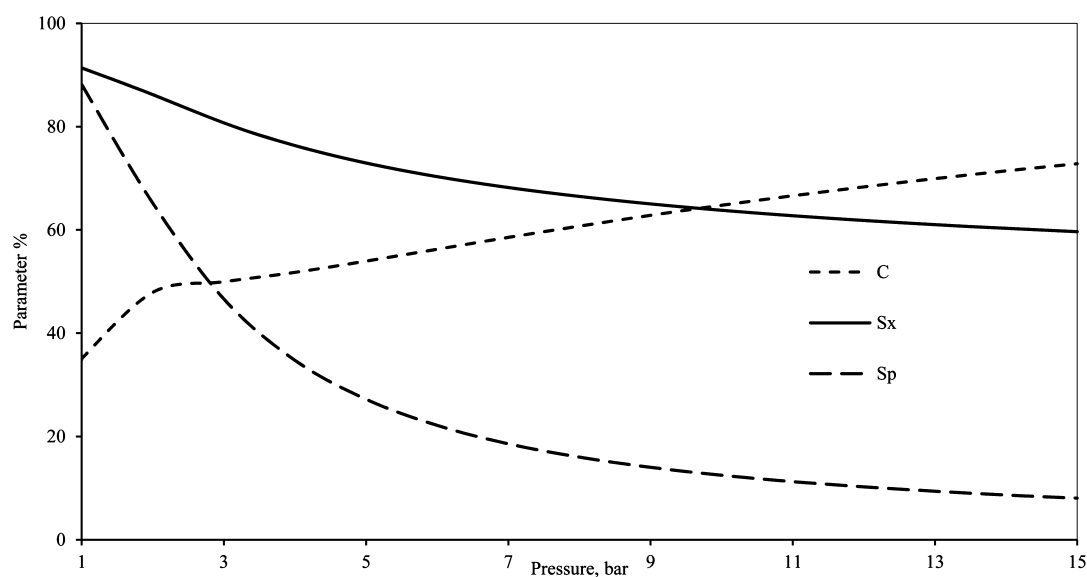


Figure 4. Effect of pressure on conversion, total xylenes selectivity, and *p*-xylene selectivity (temperature = 500 °C, $F_{T0}/F_{M0} = 1$, $W_{cat.}/F_{T0} = 15$ (g h)/mol).

from 82.4% to 40%. The optimized values of temperature and space time are lower than the starting values, which shows that the optimization results are in agreement with the sensitivity analysis findings. Based on these results, a downstream process is developed to separate *p*-xylene from the reaction products.

Objective: maximize

$$S_p = \left(\frac{F_{p-X}}{F_{p-X} + F_{m-X} + F_{o-X}} \right) \times 100 \quad (6)$$

Objective constraint:

$$\begin{aligned} \% \text{ methanol loss} &= \frac{\text{methanol reacted to form other than } p\text{-xylene}}{\text{total methanol reacted}} \\ &\times 100 \leq 40 \end{aligned} \quad (7)$$

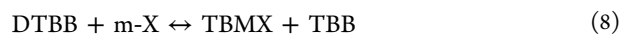
4. PROCESS FLOW DIAGRAM DEVELOPMENT

Based on the optimization results of section 3, a process is developed for the production of high purity *p*-xylene by methylation of toluene. The Peng–Robinson (PR) equation of state has been widely used in modeling hydrocarbon systems. The Aspen Plus process simulator is used with the Peng–Robinson property method for simulation as it is one of the recommended property methods by Aspen Plus Property Method Selection Assistant²³ for hydrocarbons. The gas phase contains water and methanol in addition to hydrocarbons. For the two polar compounds, water and methanol, the Peng–Robinson equation of state (PR-EOS) interaction parameters are available in the Aspen Property Data Bank.²³ For modeling liquid–liquid separation in the decanter, the nonrandom two-liquid (NRTL) property method is used as the Aspen Plus Property Data Bank²³ has all the interaction parameters among polar compounds (water and methanol) and the nonpolar aromatics. RadFrac block is used

Table 5. Stream Data for *p*-Xylene Production from Methylation of Toluene

stream name		toluene	methanol	S-5	S-6	S-8	S-12	S-13	S-14	S-14A	S-15
mole flow	kmol/h	215.24	393.65	1538.89	1609.77	96.13	437.16	1078.28	123.91	4.09	306.82
mass flow	kg/h	19831.89	12613.52	110549.50	110549.50	2931.66	9638.41	97751.62	3889.47	120.29	5551.94
vapor fraction		0.00	0.00	1.00	1.00	1.00	0.00	0.00	0.00	1.00	0.00
temperature	°C	25.00	25.00	399.95	400.00	50.00	49.46	44.38	70.87	70.87	145.09
pressure	bar	1.01	1.01	3.00	2.99	1.20	10.50	8.50	4.00	4.00	4.20
Component Mole Flow											
Toluene	kmol/h	215.24	0.00	1000.00	804.05	5.70	1.49	796.47	1.53	0.02	0.00
Methanol	kmol/h	0.00	393.65	500.00	172.29	6.21	114.55	54.18	108.39	1.23	1.75
<i>p</i> -X	kmol/h	0.00	0.00	18.31	204.52	0.56	0.13	200.91	0.13	0.00	0.00
Water	kmol/h	0.00	0.00	16.86	344.57	20.42	317.82	7.67	12.91	0.06	305.07
Benzene	kmol/h	0.00	0.00	0.33	5.33	0.11	0.01	5.02	0.01	0.00	0.00
GH	kmol/h	0.00	0.00	3.14	74.02	63.12	3.14	9.24	0.91	2.79	0.00
<i>m</i> -X	kmol/h	0.00	0.00	0.20	2.57	0.01	0.00	2.45	0.00	0.00	0.00
<i>o</i> -X	kmol/h	0.00	0.00	0.05	2.42	0.01	0.02	2.34	0.02	0.00	0.00
TBB	kmol/h	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DTBB	kmol/h	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TBMX	kmol/h	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
stream name		S-16	S-16A	S-17	S-19	S-21	S-22	solvent	S-23	S-24	S-25
mole flow	kmol/h	75.23	8.77	994.28	192.28	925.91	184.00	3.00	11.28	5.00	179.00
mass flow	kg/h	2993.19	260.28	94498.15	20412.77	77974.83	19489.30	514.88	1438.36	486.52	19002.78
vapor fraction		0.00	1.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
temperature	°C	74.25	74.25	212.83	187.37	400.00	136.99	150.00	156.56	78.13	113.94
pressure	bar	8.00	8.00	8.20	3.20	3.00	1.00	1.50	1.10	0.40	0.50
Component Mole Flow											
toluene	kmol/h	7.87	0.08	788.51	0.10	789.95	0.10	0.00	0.00	0.04	0.06
methanol	kmol/h	52.90	1.29	0.00	0.00	108.39	0.00	0.00	0.00	0.00	0.00
<i>p</i> -X	kmol/h	0.00	0.00	200.91	187.55	13.49	181.98	0.00	5.57	3.40	178.59
water	kmol/h	7.55	0.12	0.00	0.00	12.91	0.00	0.00	0.00	0.00	0.00
benzene	kmol/h	4.85	0.10	0.07	0.00	0.08	1.57	0.00	0.00	1.56	0.01
GH	kmol/h	2.06	7.18	0.00	0.00	0.91	0.00	0.00	0.00	0.00	0.00
<i>m</i> -X	kmol/h	0.00	0.00	2.45	2.32	0.14	0.00	0.00	0.00	0.00	0.00
<i>o</i> -X	kmol/h	0.00	0.00	2.34	2.32	0.04	0.34	0.00	1.97	0.00	0.34
TBB	kmol/h	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.16	0.00	0.00
DTBB	kmol/h	0.00	0.00	0.00	0.00	0.00	0.00	2.00	1.26	0.00	0.00
TBMX	kmol/h	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.31	0.00	0.00

the case of crystallization as crystallizing out 97.5% of a stream is not feasible. The other option for xylene separation is by distillation. *o*-Xylene can be separated from *p*-xylene by extensive distillation as the relative volatility is around 1.17. *m*-Xylene and *p*-xylene, however, can be hardly separated by ordinary distillation due to a relative volatility of around 1.02. Saito et al.²⁴ reported the separation of *m*-xylene from *p*-xylene by reactive distillation. *m*-Xylene reacts preferentially with di-*tert*-butyl-benzene (DTBB) and *tert*-butyl-benzene (TBB) to form *tert*-butyl *m*-xylene (TBMX) and benzene (B). For modeling the reactive distillation column in the Aspen Plus, the reactions can be considered to reach equilibrium²⁵ as in Venkataraman²⁷, based on the experimental work of Saito et al.²⁶ Equilibrium data is given by Saito et al.²⁴ The reactions are shown in eqs 8 and 9,^{24,25} and the corresponding equilibrium constants are given in eqs 10 and 11, respectively.²⁴



$$K_9^R = \frac{x_{\text{TBMX}}x_{\text{TBB}}}{x_{\text{DTBB}}x_{m\text{-X}}} = 0.6 \quad (10)$$

$$K_{10}^R = \frac{x_{\text{TBMX}}x_{\text{B}}}{x_{\text{TBB}}x_{m\text{-X}}} = 0.16 \quad (11)$$

The mixed xylene stream S-19 is fed to reactive distillation column DST-103. The standard inside-out algorithm by Boston and Britt²³ is used for convergence. The column operates at 1 bar, which results in a suitable temperature in the condenser, 137 °C, so that cooling water can be used as a coolant. The equilibrium reactions shown in eqs 8 and 9 are added to the distillation block. The solvent stream containing DTBB and TBB is added at the 10th stage (from the top) of the distillation column. Separation of *o*-xylene requires a large number of trays, a high reflux ratio, and a high reboiler duty. To get optimum results, a sensitivity analysis is made. The mole fraction of *p*-xylene in the distillate and the mole fraction of *o*-xylene in the bottom are set using the design specifications tool within the RadFrac environment as 0.99 and 0.16, respectively. These composition values result in 99.7% *p*-xylene purity in the product stream S-25. The reflux ratio and distillate rate are varied to get the set values of compositions in the column top and bottom. For each set of the total number of equilibrium stages (including condenser and reboiler) and feed stage location, the RadFrac block converges only if the design spec tool also converges. Then, the NQ Curves tool, available in RadFrac block,²¹ is used to find the optimum location of the feed stage that gives the minimum reboiler duty. The results of this analysis are shown in Table 6 for a range 40–60 for the total number of equilibrium stages.

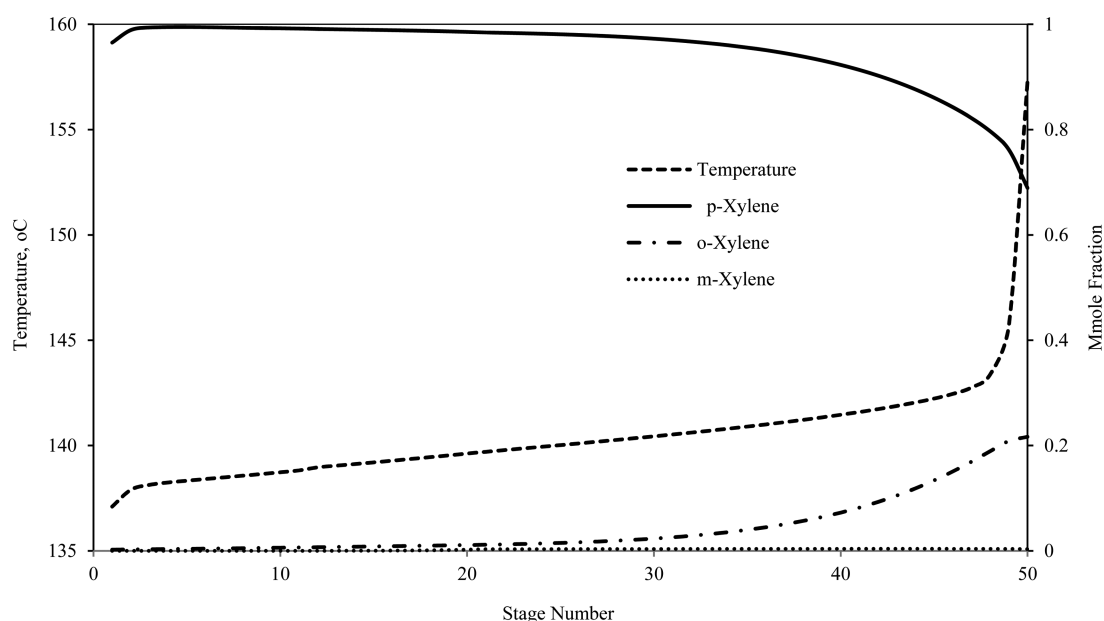


Figure 6. Temperature and composition profiles of *m*-xylene, *o*-xylene, and *p*-xylene in reactive distillation column DST-103.

Table 6. Results of NQ Curves Analysis for Reactive Distillation Column DST-103

DST-103 sensitivity analysis					
number of stages	feed stage location	molar reflux ratio	distillate rate, kmol/h	reboiler duty, Gcal/h	<i>p</i> -xylene product purity, wt %
40	21	22.95	183.78	37.80	0.997
45	20	11.19	183.74	18.97	0.997
50	21	7.99	183.72	13.85	0.997
55	21	7.18	183.70	12.55	0.997
60	21	6.63	183.70	11.68	0.997

As shown in the table, there is a trade-off between the total number of equilibrium stages and the reboiler duty. Using more than 50 equilibrium stages does not result in any significant decrease in reboiler duty, so 50 equilibrium stages are used along with a feed stage location of 21 in DST-103. Figure 6 shows the temperature and composition profiles of *o*-xylene and *m*-xylene in DST-103 (stage number is counted from top to bottom). The composition of *m*-xylene decreases due to reaction with DTBB and TBB while composition of *o*-xylene drops due to high reflux ratio (7.99) and high reboiler duty (13.85 Gcal/h). Distillate stream S-22 contains almost no *m*-xylene and most of *o*-xylene is also separated, but it has the produced benzene, which lowers the purity. S-22 is sent to distillation column DST-104 where the light component, benzene, is separated. The product stream S-25 comes from the bottom of DST-104 and meets the purity specification of 99.7%.

6. CONCLUSION

p-Xylene is typically produced by catalytic re-forming of naphtha.³ In the process developed, shown in Figure 5, *p*-xylene production is increased by converting toluene to *p*-xylene by reaction with methanol using Mg modified ZSM-5 catalyst.¹⁹ The reaction is followed by separation of *p*-xylene to meet the required purity.¹⁹ To simulate toluene methylation in PBR-100, the kinetic model by Valverde²⁰ is used and for the reactive distillation column, DST-103, chemical reactions are considered to reach equilibrium as in Venkataraman,²⁵ based on

the experimental work of Saito et al.²⁴ The optimized reaction conditions in PBR-100, producing high purity *p*-xylene, are determined. Operating the reactor at low temperature, low pressure, and low contact time is found to enhance *p*-xylene selectivity. The enhancement of *p*-xylene selectivity at low contact time is in agreement with the experimental results reported in Sotelo et al.¹⁹ and Breen et al.⁸ A toluene to methanol feed ratio of 2 slightly lowers conversion but significantly reduces methanol loss by side reactions.

The separation cost of *p*-xylene is likely to be significantly reduced due to the highly selective reactor and the use of reactive distillation to separate *p*-xylene. The product of the process is 99.7% pure *p*-xylene with an overall 83% conversion of toluene to *p*-xylene. Due to increasing demand for *p*-xylene this process is proposed as an alternative to produce *p*-xylene efficiently.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

[†]Part of this work will be presented in the 44th IUPAC World Chemistry Congress.

NOMENCLATURE

- A_i = pre-exponential factor, mol/(g·h·atm²) or mol/(g·h·atm)
- C = toluene conversion, %
- k_i = rate constant, mol/(g·h·atm²) or mol/(g·h·atm)
- E_i = activation energy, kJ/mol
- η_i = effectiveness factor, –
- p = pressure, atm
- K_i^R = equilibrium constant, –
- S_x = xylene selectivity, %
- S_p = *p*-xylene selectivity, %
- F_{T_o} = toluene molar flow rate, kmol/h
- F_{M_o} = methanol molar flow rate, kmol/h
- $W_{cat.}$ = catalyst weight, g

Subscripts

- i = reaction number
- T = toluene
- M = methanol

o = feed
cat. = catalyst

Compounds

B = benzene
DTBB = di-*tert*-butyl-benzene
GH = light gaseous hydrocarbons
M = methanol
m-X = *m*-xylene
o-X = *o*-xylene
p-X = *p*-xylene
T = toluene
TBB = *tert*-butyl-benzene
TBMX = *tert*-butyl *m*-xylene
W = water

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