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Intensified *P*-xylene Production Process through Toluene and Methanol Alkylation

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Abstract

The production of *p*-xylene has received more and more attention since it is widely used in chemical synthetic resins, pharmaceutical, chemical fiber, and pesticides industries. The *p*-xylene production through toluene alkylation is considered to be more promising due to high selectivity of *p*-xylene and little environmental impact compared to other methods. Although the existing *p*-xylene production process through toluene alkylation could achieve high selectivity of *p*-xylene, the methanol conversion is still as low as 70.0 %, requiring methanol recovery and recycle system and resulting in additional loss of toluene in the downstream separation of light component, methanol and toluene. Based on these findings, an intensified *p*-xylene production process through toluene alkylation with complete methanol conversion is proposed and simulated using Aspen Plus V8.4®. The optimal operating conditions for the alkylation reactor are obtained using the sensitivity analysis tool and sequential quadratic programming (SQP) optimization solver in Aspen Plus V8.4®. It is found that the methanol conversion could reach 98.0 % with *p*-xylene selectivity of 92.0 % through increasing reaction temperature to 442.5 °C and pressure to 4.0 bar compared to the existing process, resulting in the removal of methanol recovery and recycle system and less toluene loss in the downstream separation. The comparative evaluations demonstrate that the proposed process is more efficient than the existing process based on economic and environmental metrics. The overall TAC is reduced by 4.71 % and CO_2 emissions are decreased by 40.2 % compared to the existing process without heat integration.

Keywords: Process design, *p*-xylene, toluene alkylation, heat integration, TAC, carbon emission

1 Introduction

The production of *p*-xylene has received more and more attention from both academia and chemical industries since it is one of the most important petrochemical intermediates that is widely used in chemical synthetic resins, pharmaceutical, chemical fiber, and pesticides industries.[1-4] The demand of *p*-xylene in the world has been greatly increasing in recent years, especially from China.[5] *P*-xylene is mainly produced by selective toluene disproportionation[6-8], C_8 aromatic isomerization[9], and adsorptive separation or crystallization from other xylene isomers[10-11]. Although these methods produce high-purity *p*-xylene, relatively high cost is required because of either expensive raw materials in selective toluene disproportionation or low selectivity of *p*-xylene in C_8 aromatic isomerization. The production of *p*-xylene through adsorptive separation or crystallization requires more energy, due to very close boiling points of xylene isomers and low selectivity of *p*-xylene.[11] Meanwhile, these production processes are associated with the generation of a considerable amount of by-products (e.g., ethylbenzene) resulting in environmental pollution.

With the significant reduction of toluene price arising from great increase of its global productivity[12], the selective alkylation using toluene as a feedstock for synthesis of *p*-xylene has been identified as a promising alternative.[13-17] The toluene is reacted with another feedstock methanol to produce *p*-xylene directly. Side reactions could also take place simultaneously to generate *m*-xylene and *o*-xylene. Unreacted toluene and methanol are recovered in the downstream distillation processes and recycled to the feed. *P*-xylene is separated from byproducts *m*-xylene and *o*-xylene in the downstream reactive distillation. Compared to other existing methods, this method requires mild reaction conditions (i.e., 400.0~500.0 °C and 3.0~4.0 bar) and could result in high utilization of toluene with excessive methanol and high selectivity of *p*-xylene.[13-17] However, this production process is viable only when the cost of methanol is low (e.g., < $ 0.35/ton) and the selectivity of *p*-xylene is high enough (e.g., > 90.0 %).[18,35]

To reach high selectivity of *p*-xylene in toluene methylation, Breen et al.[18,19] and Sotelo et al.[20] found out the selectivity of Mg-modified ZSM-5 catalyst to *p*-xylene can achieve as high as nearly 100 %. Zhao[21] demonstrated that high selectivity of *p*-xylene on ZSM-5 zeolite catalyst could be always obtained. High selectivity of *p*-xylene not only inhibits the production of other unwanted isomers of xylene, but also increases *p*-xylene productivity and improves process economics. Meanwhile, it has been experimentally demonstrated that methanol conversion could remain at 100 % over Mg-modified ZSM-5 catalyst even with highest magnesium content.[22-24] Ashraf et al.[15] designed a *p*-xylene production process through toluene methylation with Mg-modified ZSM-5 catalyst. Their objective is to achieve maximum selectivity of *p*-xylene and to obtain 99.7 wt % of *p*-xylene. However, the production process of *p*-xylene still requires the present situation of methanol and toluene two-component separation cycle due to incomplete reaction in the existing reactor. In addition, the separation of light component, methanol and toluene in the downstream distillation could lead to additional loss of toluene.

In order to overcome the disadvantages of Ashraf et al.[15] and improve process economics, an intensified *p*-xylene production process through toluene and methanol alkylation is proposed in this study where the methanol recovery and recycle system are cut off. A systematic design procedure for the proposed process involving thermodynamic and kinetic insights, process simulation, sensitivity analysis, and optimization through Sequential Quadratic Programming tool implemented in Aspen Plus V8.4® is proposed to identify the optimal operating conditions and reduce toluene loss in the downstream separation. Then, heat integration is conducted using pinch analysis tool implemented in Aspen Plus V8.4® to improve energy efficiency and further reduce total cost. Finally, two examples are used to illustrate the advantages of the proposed process based on economic and environmental metrics.

2 Proposed *p*-xylene production process

Figure 1 illustrates the proposed *p*-xylene production process through toluene methylation. The fresh feeds (i.e. toluene and methanol) are first preheated and then vaporized in the heating furnace before entering the alkylation reactor. In the alkylation reactor, toluene is primarily reacted with methanol to produce *p*-xylene. Other side reactions also take place such as methanol self-decomposition into hydrocarbons and water, and *p*-xylene conversion to *m*-xylene and *o*-xylene. A condenser is added to partially cooling outlet stream of the reactor to get light compounds such as gaseous hydrocarbon (GH) which are separated out in the subsequent flash column. The cooled GH is separated out at the top of flash column and the bottom liquid is fed into a decanting vessel for further separation where the upper layer product is water and the lower layer is aromatic mixture including benzene, toluene, *p*-xylene, *m*-xylene, and *o*-xylene. The aromatic mixture is separated further into benzene, toluene, *p*-xylene, and mixed aromatics through two distillation columns and one reactive distillation unit. 99.7 wt % of *p*-xylene is obtained at the top of the reactive column. Compared to the existing process[15] which is depicted in Figure 2, the proposed process does not require methanol recovery and recycle system due to almost complete conversion of methanol. Therefore, a trace amount of methanol in the reactor effluent could be found in the proposed process, whilst non-negligible amount of unconverted methanol existed in the reactor effluent in the existing process reported in the literature.[15]

PLEASE INSERT FIGURE 1 HERE

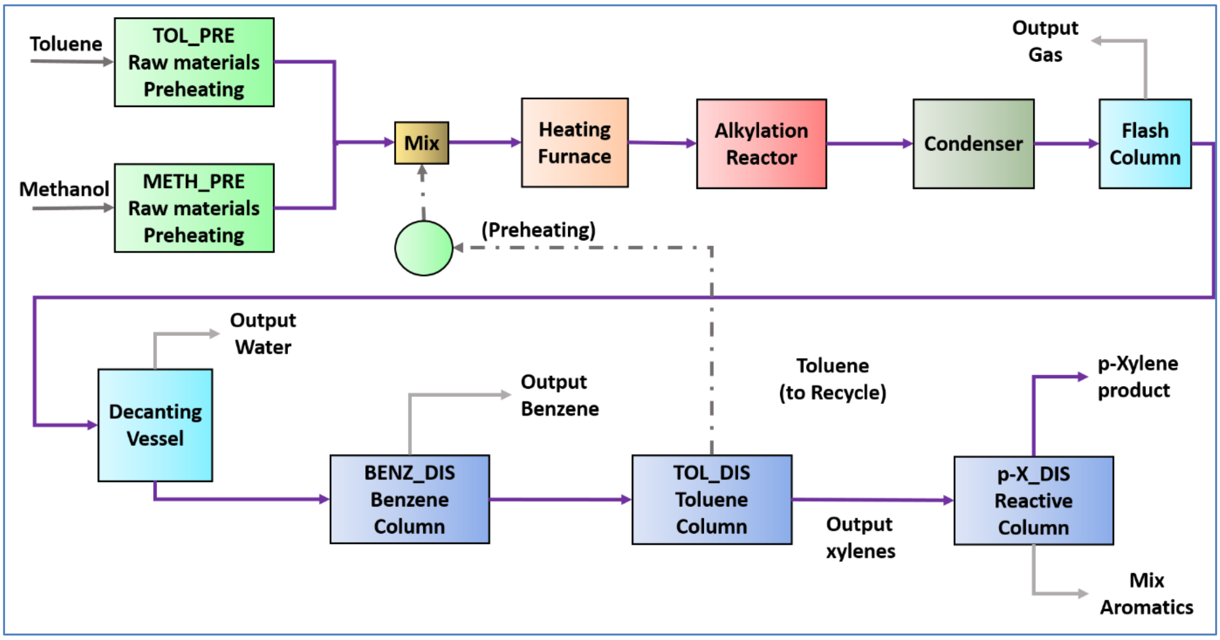

Figure 1 The proposed *p*-xylene production process through toluene methylation with complete conversion of methanol

PLEASE INSERT FIGURE 2 HERE

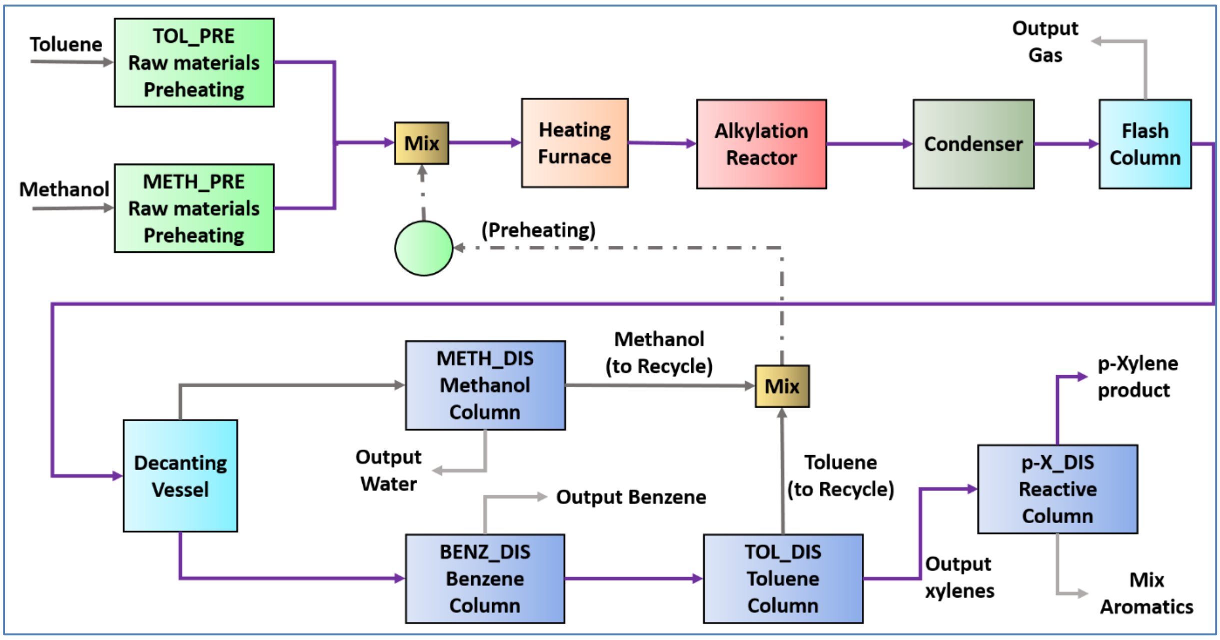

Figure 2 The existing *p*-xylene production process by toluene methylation[15]

2.1 Reaction kinetics in alkylation reaction

In the alkylation reactor, toluene is primarily reacted with methanol to produce *p*-xylene. It has been shown that methanol is completely converted in the temperature range of 400 – 600 oC.[24-25] Mantha et al.[26] and Bhat et al.[27] developed a kinetic model based on the Langmuir-Hinshelwood approach, ignoring other products than xylene generated from the side reactions of methanol. Vayssilov et al.[28] proposed a power law kinetic model only considering the reactions of toluene alkylation and xylene isomerization. However, the experimental data that were used for kinetic model development is generated at a unique temperature of 227 °C. Sotelo et al.[20] developed a kinetic model over the Mg-modified catalysts in a fixed-bed reactor with the consideration of diffusional effects and the influence of *p*-xylene isomerization over the external zeolite surface, reproducing the experimental product distribution with an average relative error of 6.8%. Valverde et al.[25] developed a simple power law kinetic model for toluene alkylation with methanol over Mg-modified

ZSM-5 catalyst considering all possible side reactions of methanol. The catalyst used contains 1.09 wt% Mg and 35 wt% sodium montmorillonite as a binder with an average particle size of 0.75 mm. The reaction kinetic model[25] is introduced as follows,

$$\text{Toluene} + \text{Methanol} \rightarrow \text{p} - \text{Xylene} + \text{Water} \qquad \text{r}_1 = k_1 p_\text{T} p_\text{M} \tag{1}$$

$$2\text{Methanol} \rightarrow \text{GH} + 2\text{Water} \qquad \text{r}_2 = k_2 p_\text{M}^2 \tag{2}$$

$$\text{Toluene} \rightarrow \frac{1}{2}\text{Benzene} + \frac{1}{2}\text{p} - \text{Xylene} \qquad \text{r}_3 = k_3 p_\text{T} \tag{3}$$

$$\text{p} - \text{Xylene} \rightarrow \text{Toluene} + \frac{1}{2}\text{GH} \qquad \text{r}_4 = k_4 p_{\text{p}-\text{X}} \tag{4}$$

$$\text{p} - \text{Xylene} \rightarrow \frac{1}{2}(\text{m} - \text{Xylene} + \text{o} - \text{Xylene}) \qquad \text{r}_5 = k_5 p_{\text{p}-\text{X}} \tag{5}$$

where, k_i denotes rate constant and p represents partial pressure. Gaseous hydrocarbons (GH) indicate light species (e.g., methane, ethane, ethylene, propane, and butanes), which is represented as pure ethylene to ensure stoichiometric balance in eq. 2. The kinetic parameters are given in Table 1.

PLEASE INSERT TABLE 1 HERE

Table 1 Kinetic parameters of toluene methylation over Mg-modified ZSM-5 zeolite catalyst[25]

reaction	pre-exponential factor, A_i, mol/(g h atm^2) or mol/(g h atm)	activation energy, E_i, (kJ/mol)
1	403 ± 5	45.7 ± 0.4
2	1346 ± 64	50.6 ± 0.5
3	96.2 ± 1	59.0 ± 0.5
4	0.3815 ± 0.05	19.6 ± 0.7
5	46.94 ± 0.5	48.9 ± 0.3

The kinetic rate constant k_i is related to A_i and E_i as Eq. 6.

$$k_i = A_i T^n e^{\frac{-E_i}{RT}} \tag{6}$$

It is shown that the reactions given in eqs. 1, 3, and 4 occur preferentially inside pores of the catalyst. Consequently, the effectiveness factors η_1, η_3, and η_4 are used to account for diffusion limitations.[25] The values of the effectiveness factors, η_3 and η_4 are given in Table 2 for three different temperatures: 460.0 °C, 500.0 °C, and 540.0 °C. The value of effectiveness factor η_1 is 0.98 which is approximated to be 1.

PLEASE INSERT TABLE 2 HERE

Table 2 Effectiveness factors for toluene methylation over Mg modified ZSM-5 catalyst[25]

temperature, °C	η_3	η_4
460.0	0.7781 ± 0.117	2.977 ± 1.10
500.0	0.5335 ± 0.170	3.212 ± 0.59
540.0	0.4470 ± 0.320	3.201 ± 0.97

The aforementioned reaction kinetic model with the given parameter values[25] are quantitatively validated by Ashraf et al.[15] The simulation results are in agreement with the experimental results from Sotelo et al.[20] The same reaction kinetic model was also used to investigate the effects of temperature, pressure, space time and toluene-to-methanol feed ratio on toluene conversion, xylene selectivity and p-xylene selectivity using the sensitivity analysis feature in Aspen Plus and obtain the best reaction conditions including temperature and pressure.[29] It should be noted that although the kinetic parameters and effectiveness factors were reported in three temperatures 460 °C, 500 °C and 540 °C, they are valid for the temperatures ranging from 400 °C to 540 °C and for the pressures ranging from 1 to 15 bar as indicated in the sensitivity analysis of Ashraf et al.[15] Hence, the same kinetic model with the given parameter values are also used in this work. The mean values for each of parameters given in Tables 1 are input directly. However, for the data in Table 2, the specific effectiveness factors corresponding to other temperatures are not given and then these factors are calculated based on the Eqs. S1-S4 and the iterative algorithm block diagram of calculating effectiveness diffusion coefficient De as illustrated in Figure S1 of Supporting

Information.

2.2 Reaction kinetics in reactive distillation

It is well known that *p*-xylene and *m*-xylene are difficult to separate using conventional distillation since they have very close boiling point at 1.0 bar as shown in Table 3. However, *m*-xylene can be selectively *tert*-butylated (reaction with di-tert-butyl-benzene) in the presence of aluminum chloride under mild alkylation conditions to form *tert*-bytyl *m*-xylene (TBMX) with higher boiling point as shown in Table 3, which can be separated from *p*-xylene. When modeling the reactive distillation column in Aspen Plus, the reactions can be considered to reach equilibrium as reported in the work of in Venkataraman[30], based on the experimental work of Saito et al.[31] The reaction equations are presented in eqs. 7-8. The corresponding equilibrium constants are given in eqs. 9-10, respectively.

$$\mathrm{DTBB} + \mathrm{m-X} \rightarrow \mathrm{TBMX} + \mathrm{TBB} \tag{7}$$

$$\mathrm{TBB} + \mathrm{m-X} \rightarrow \mathrm{TBMX} + \mathrm{B} \tag{8}$$

$$K_1^R = \frac{x_{TBMX}\, x_{TBB}}{x_{DTBB}\, x_{m-X}} = 0.6 \tag{9}$$

$$K_2^R = \frac{x_{TBMX}\, x_{B}}{x_{TBB}\, x_{m-X}} = 0.16 \tag{10}$$

In the equations above, DTBB represents di-*tert*-butyl-benzene, TBB refers to *tert*-butyl-benzene, TBMX is *tert*-butyl *m*-xylene, and benzene is abbreviated to B. Equilibrium data are given by Saito et al.[31]

PLEASE INSERT TABLE 3 HERE

Table 3 Boiling and freezing points of some of the materials present in the process

material	normal boiling point, °C	freezing point, °C	reference
p-X	138.3	13.3	32
m-X	139.1	-47.8	32
o-X	144.4	-25.2	32
TBMX	205.5	-17.0	32

3 Process design

The proposed process is used to produce 179.0 kmol/h *p*-xylene product with a purity of 99.7 wt % using 393.0 kmol/h fresh methanol and 215.0 kmol/h fresh toluene as feeds. Figure 3 presents the design procedure for the proposed *p*-xylene production process. First, process simulation of the existing process[15] is conducted in Aspen Plus to construct a base case. Then, optimal operating conditions in the alkylation reactor are generated through sensitivity analysis and Sequential Quadratic Programming (SQP) optimization method built in Aspen Plus. The objective is to achieve complete methanol conversion subject to some constraints such as *p*-xylene selectivity constraints. After that, heat integration is conducted to improve energy efficiency of the proposed process. Finally, the proposed process is evaluated based on the total annualized cost and carbon emissions.

PLEASE INSERT FIGURE 3 HERE

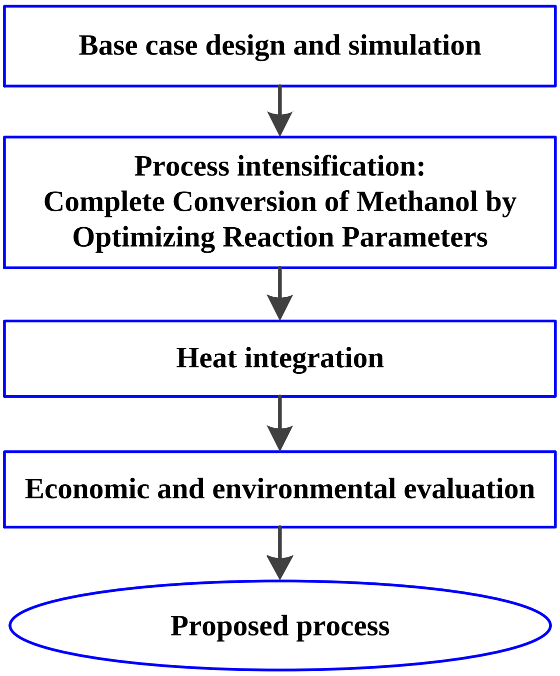

Figure 3 A systematic design procedure for the proposed *p*-xylene production process

3.1 Optimal operating conditions for the reactor

Some researchers have performed simulation of an isothermal packed bed alkylation reactor using the kinetic model of Valverde.[15,25] To ensure fair comparison, the same reactor design[15] is used here including the reactor type and size to ensure a fair comparison and demonstrate that the improvement is not contributed from changing the reactor size. The required key operating conditions for the reactor include toluene-to-methanol feed ratio *m*, temperature *T*, and pressure *P*. The objective is to maximize methanol conversion denoted as *z*, which is represented below:

$$\mathrm{z} = \left(\frac{\text{inlet methanol-outlet methanol}}{\text{inlet methanol}}\right)\times 100 \tag{11}$$

Subject to a set of constraints as follows:

The outlet flow rate of *p*-xylene from the reactor should exceed the minimum value of 187.0 kmol/h reported by Ashraf et al.[15]:

$$F_{p-X} \geq F_{p-X}^{\min} \tag{12}$$

The concentration of methanol in the alkylation reactor effluent should be less than a maximum concentration, which is assumed to be 0.3 wt %:

$$M\% \leq M\%^{\max} \tag{13}$$

The *p*-xylene selectivity (denoted as $S_{p\text{-}X}$) should also exceed a minimum value of selectivity, which is assumed to be 90.0 %:

$$S_{p-X} = \left(\frac{F_{p-X}}{F_{p-X}+F_{m-X}+F_{o-X}}\right)\times 100 \geq S_{p-X}^{\min} \tag{14}$$

The toluene conversion should exceed a minimum value, which is about 23.0 %:

$$X_{\text{toluene}} = \left(\frac{\text{inlet toluene-outlet toluene}}{\text{inlet toluene}}\right)\times 100 \geq X_{\text{toluene}}^{\min} \tag{15}$$

Besides eqs. 12-15, there are also other constraints such as mass and energy balances, which is implicitly implemented in Aspen Plus.

In addition, the toluene-to-methanol feed ratio m, temperature T, and pressure P must meet their lower and upper bounds, as described by the following equations:

$$m^L \le m \le m^U \tag{16}$$

$$T^L \le T \le T^U \tag{17}$$

$$P^L \le P \le P^U \tag{18}$$

The lower and upper bounds of the toluene-to-methanol feed ratio, temperature, and pressure can be determined based on sensitivity analysis tool implemented in Aspen Plus. The objective function and the constrains are expressed in Fortran statement in Aspen plus and solved using SQP optimization solver implemented in Aspen Plus.

3.2 Economic evaluation

The total annual cost (TAC), which consists of total operating cost (TOC) and total capital investment (TCI), is used to evaluate the economics of both the proposed process and the existing process.[15] The TAC is defined in eq. 19.[33] Following the suggestion of Turton et al.[34], the shorter the payback period, the more profitable the project. Thus, a three-year payback period is taken in calculating TAC and the total annual operating time is assumed to be 7920 h/year.

$$\mathrm{TAC} = \frac{\mathrm{TCI}}{payback\ period} + \mathrm{TOC} \tag{19}$$

where, the TCI mainly involves equipment purchase cost (pump, heat, reactor, flash, decanter, and distillation columns) and the installation cost of the equipment, and the TOC mainly consists of utility cost (e.g., cost of steam, cooling water, and electricity used in heat exchangers, pumps and furnace) and raw materials cost. The economic data for raw materials and utilities are given in Table 4. The inlet and outlet temperatures of cooling water are assumed to be 20 °C and 25 °C. Pipe and valves costs are neglected because they are much lower than utility and raw material cost. Note that TCI is directly calculated using Aspen Process Economic Analyzer V8.4® by importing flowsheet simulation results in Aspen Plus simulator. The calculation of TOC is much more complicated. To simplify the calculation, two assumptions are made. First, the fixed operating cost is not taken into account in the calculation of the TOC. Second, the cost of the additional DTBB and TBB that are used in the RD is not considered because their amount and cost is very small in terms of equipment and energy cost. It should be also noted that these two assumptions have no effect on the final comparative results due to the same amount of *p*-xylene produced in both the proposed process and the existing process.

PLEASE INSERT TABLE 4 HERE

Table 4 Economic data for raw materials and utilities

component	price	unit	reference
raw materials			
toluene	770.0	\$/t	35
methanol	380.0	\$/t	35
utilities			
fuel	9.83	\$/GJ	36
LP steam (6 bar, 160 °C)	7.78	\$/GJ	36
MP steam (11 bar, 184 °C)	8.22	\$/GJ	36
HP steam (42 bar, 254 °C)	9.83	\$/GJ	36
cooling water	0.10	\$/GJ	45
electricity	0.09	\$/kWh	45

4 Results and Discussions

4.1 Base case

As mentioned earlier, the existing *p*-xylene production process proposed by Ashraf et al.[15] is used as our base case. The process flowsheet is illustrated in Figure 4. The detailed stream information is presented in Table S1 of Supporting Information. Table 5 provides a summary of the economic evaluation results from Aspen Process Economic Analyzer V8.4® where CI is capital investment and OC is the associated operating cost. The CI is obtained by the summation of equipment cost and labor cost associated with the project preparation (e.g., installation bulks) while equipment cost is bare equipment cost associated with material. Moreover, the equipment cost is the main cost in the project preparation.

It can be concluded that the utility cost for raw materials heating accounts for 35.2 % of TOC, whilst it accounts for 64.7 % of TOC for the distillation separation system. Note that the overall reaction is exothermic. Thus, cooling water is used to maintain constant reaction temperature at 400 ^{o}C. Note that the cooling water cost for the reactor is negligible compared to the utility cost for raw material heating and distillation separation system.

PLEASE INSERT FIGURE 4 HERE

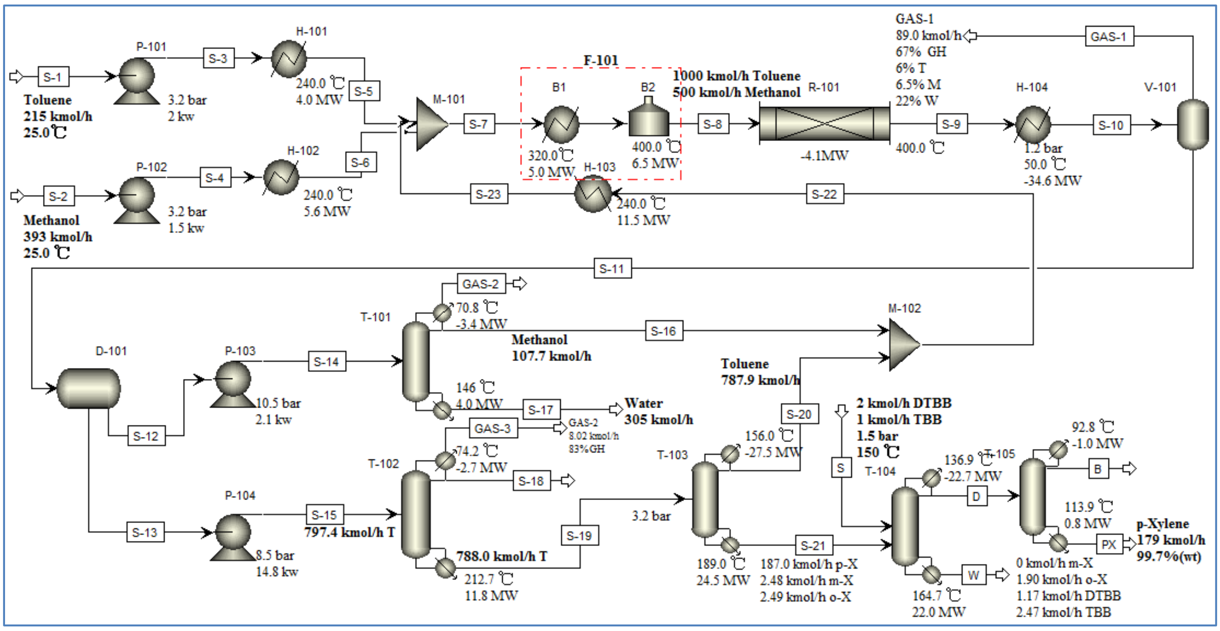

Figure 4 Process flow diagram for the base case

PLEASE INSERT TABLE 5 HERE

Table 5 Economic evaluation results for the base case

equipment	comments	value	CI (k$)	OC(k$/year)
P-101 (kw)	toluene pump	2.0	43.9	1.5
P-102 (kw)	methanol pump	1.5	42.0	1.0
P-103 (kw)	feed pump	2.1	60.9	3.2
P-104 (kw)	feed pump	14.8	76.3	25.1
H-101 (MW)	heater	4.0	133.9	1123.8
H-102 (MW)	heater	5.6	155.3	1569.6
H-103 (MW)	heater	11.5	271.7	3236.4
H-104 (MW)	condenser	34.6	392.3	98.6
F-101 (MW)	fired furnace	10.3	1520.7	2998.6
R-101 (MW)	alkylation reactor	4.1	373.0	11.7
V-101	flash vessel	-	214..1	-
D-101	decanter	-	213.3	-
T-101 ([a]C/R, MW)	methanol distillation column	3.4/4.0	792.0	948.5
T-102 (C/R, MW)	benzene distillation column	2.7/11.8	2334.3	3318.7
T-103 (C/R, MW)	toluene distillation column	27.5/24.5	4024.1	6943.9
T-104 (C/R, MW)	reaction distillation column	22.7/22.0	4562.7	5233.7
T-105 (C/R, MW)	p-xylene distillation column	1.0/0.8	734.9	147.1
total	-	-	15731.3	22661.4

[a]C represents Condenser and R represents Reboiler

It is also observed that there is a significant difference between condenser and reboiler duties in the benzene distillation column (T-102). The main possible reason is that there are a large amount of heavy components but small amount of light components in the feed to T-102. Therefore, much less distillate is obtained than that in the bottom, leading to much fewer duties required on the top and much more duties required in the bottom. In addition, the partial condenser rather than total condenser is used on the top for the separation of small amount of GH gases in the feed, which further reduces duties required in the condenser.

4.2 Optimal operating conditions for the reactor

Sensitivity analysis is conducted to investigate the effect of the three important operating parameters including the toluene-to-methanol feed ratio, operating temperature and pressure on methanol conversion, toluene conversion and p-xylene selectivity. Figure 5 illustrates the effect of the toluene-to-methanol feed ratio, m, on methanol conversion rates, C_M, toluene conversion rates, C_T, p-xylene selectivity, $S_{P\text{-}X}$ and p-xylene flowrate, $F_{P\text{-}X}$. From Figure 5, it can be observed that the methanol conversion decreases along with the increase of m. The main possible reason is that the increase of m could lead to the decrease of the space time (weight of catalyst per unit feed flowrate of toluene, $W_{cat.}/F_T$, (g h)/mol), which may decrease the reaction degree of methanol. From Figure 5, it can also be seen that when m increases, the p-xylene selectivity is increased due to ultralow residence time of p-xylene, which is in good agreement with those reported in the literature.[18-20] In other words, although the conversion of methanol can reach 98.7% when m = 1, the p-xylene selectivity is a bit low without satisfying its minimum requirement (187 kmol/h). In summary, it is very difficult to achieve the complete conversion of methanol and keep high p-xylene selectivity simultaneously by only adjusting the value of the toluene-to-methanol feed ratio, m.

PLEASE INSERT FIGURE 5 HERE

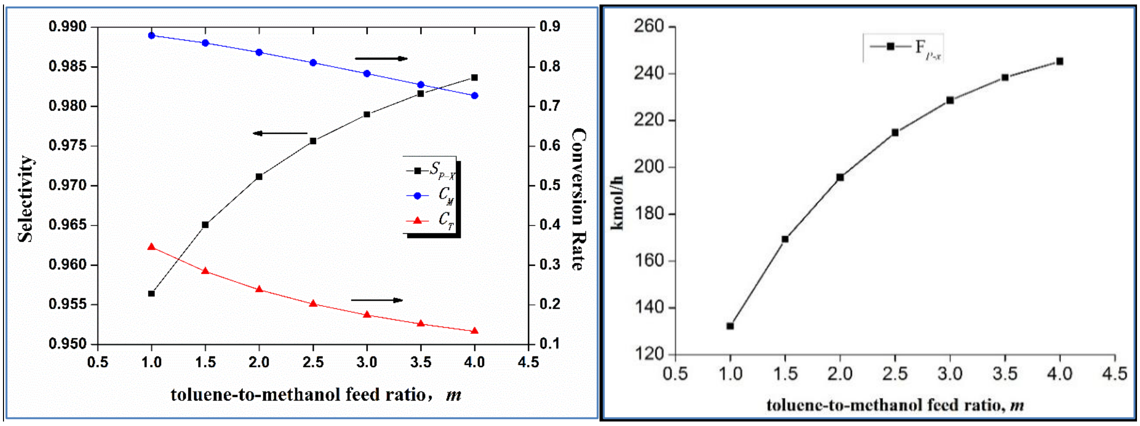

Figure 5 Effect of the toluene-to-methanol feed ratio, m, on methanol conversion rates, C_M, toluene conversion rates, C_T, p-xylene selectivity, $S_{P\text{-}X}$, and p-xylene flowrate, $F_{P\text{-}X}$ where T_R = 400.0 °C, and P_R = 3.0 bar

In thermodynamic studies on toluene alkylation with methanol, Wang et al.[37] found the alkylation of benzene, toluene and methanol, carbon deposition of toluene and methanol, and methanol self-transformation can take place spontaneously and irreversibly in forward direction. Methanol could be almost completely converted into low-carbon olefins and water during methanol self-transformation. Dung et al.[38] and Mehran et al.[39] concluded that low temperature and high pressure could inhibit the occurrence of side-chain alkylation of toluene, whilst high temperature and low pressure is favorable for inhibiting the occurrence of alkylation of toluene with light olefins. In addition, they found that the maximum toluene conversion and *p*-xylene selectivity was obtained around 427.0 °C.

Experimental results demonstrate that methanol conversion rate could reach around 100 % during the temperature range of 400.0~600.0 °C.[22-24] Meanwhile, as illustrated by Ashraf et al.[15], the selectivity of both xylene and *p*-xylene is more sensitive to the operating pressure. When the pressure is increased to 4.0 bar, the corresponding *p*-xylene selectivity decreases significantly although its conversion increases. Therefore, there is a trade-off between selectivity and conversion, providing an opportunity to achieve higher conversion with some minimum selectivity through optimization. The temperature and pressure of the reactor at 400.0~500.0 °C, 3.0~4.0 bar, respectively, are chosen as the optimization range.

The influences of the operating temperature and pressure on *p*-xylene selectivity and conversion rates of toluene and methanol are shown in Figures 6 and 7a–b, respectively.

PLEASE INSERT FIGURE 6 HERE

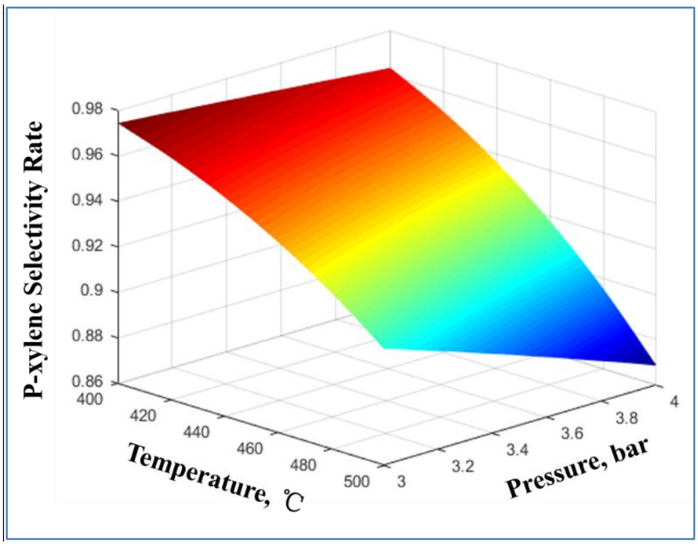

Figure 6 Effect of temperature and pressure on *p*-xylene selectivity when *m* = 2

PLEASE INSERT FIGURE 7 HERE

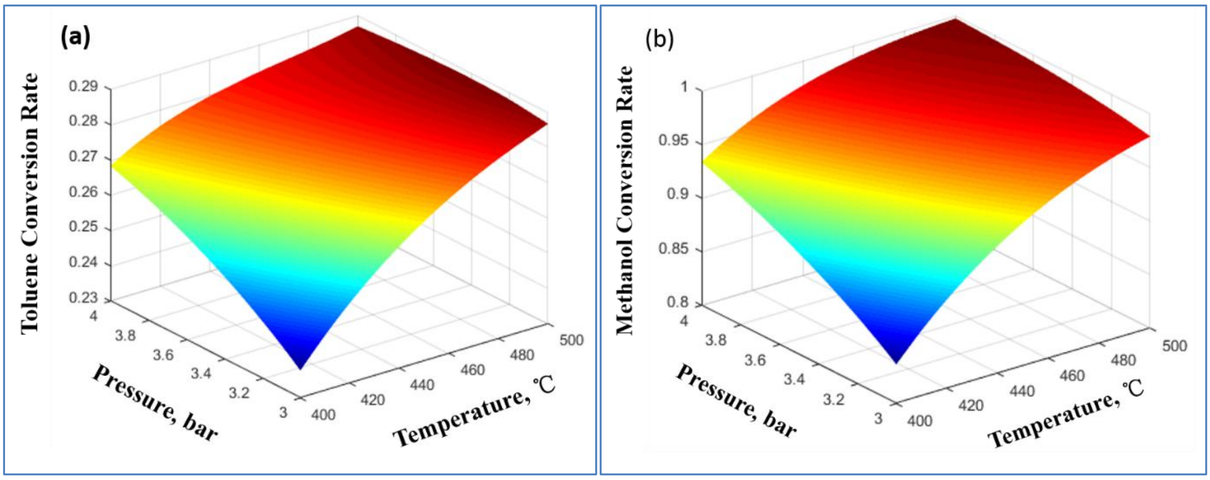

Figure 7 Effect of temperature and pressure on: **(a)** toluene conversion rate and **(b)** methanol conversion rate when *m* = 2

As shown in Figure 6, the selectivity of *p*-xylene decreases along with the increase in temperature and pressure. When the temperature is 500.0 ℃ and the pressure is 4.0 bar, the selectivity of *p*-xylene reaches only around 85.0 %, and the remaining 15.0 % are isomerization products (i.e., *o*-xylene and *m*-xylene). However, as the temperature decreases to 400.0 ℃ and the pressure changes to 3.0 bar, the selectivity of *p*-xylene can achieve above 97.0 %. From Figure 7a, the toluene conversion rate increases with the increase of temperature and pressure, demonstrating both temperature and pressure are key factors in toluene alkylation. It can be seen from Figure 7b that the methanol conversion rate increases with the increase of the temperature and pressure and can reach 99.9 % at 500.0 °C and 4.0 bar. Therefore, it can be concluded that the main reaction involving toluene alkylation, the isomerization of *p*-xylene, and the conversion of methanol to hydrocarbons prefer high temperature and pressure.

Based on the above analysis, the lower and upper bounds of the operating temperature, pressure and toluene-to-methanol feed ratio, *m*, are thus obtained, as shown in Table 6.

PLEASE INSERT TABLE 6 HERE

Table 6 Lower and upper bounds of toluene-to-methanol feed ratio, temperature and pressure

operating variables	lower bounds	upper bounds
temperature, °C	400.0	500.0
pressure, bar	3.0	4.0
toluene-to-methanol feed ratio, *m*	1	4

The optimization model **PM** is solved using SQP optimization solver implemented in Aspen Plus on a desktop with Intel(R) Core(TM) i7-4790 CPU @ 3.60GHz, 8 GB memory. The optimal values are obtained within 5 minutes and they are listed in Table 7.

PLEASE INSERT TABLE 7 HERE

Table 7 Optimal operating conditions for the reactor

	T, °C	P, bar	Space time, W/F_T, (g h)/mol	*m*	$S_{p\text{-}X}$	${}^aC_T$	${}^aC_M$
Base case	400.0	3.0	2.5	2.0	97.7	23.0	65.5
optimized	442.5	4.0	3.4	1.8	92.0	28.2	98.0

${}^aC_T$ represents toluene conversion and C_M represents methanol conversion.

For a fair comparison, the production rate of *p*-xylene is maintained at 179.0 kmol/h in the proposed process, which is the same as the base case. After optimization, the reduced loss of toluene is sent back to the alkylation reactor and the conversion of toluene is increased, so that the amount of *p*-xylene can be kept same with that in base process although lower selectivity as compared with the base process. Meanwhile, in the existing process, the feed methanol for the alkylation reactor consists of two parts: one part is amount of 107.0 koml/h methanol that recovered from distillation system, the other part is amount of 393.0 koml/h fresh methanol to maintain a quantitative *p*-xylene production. However, in the optimized process, a complete reaction of methanol took place in the alkylation reactor, only a flowrate of 393.0 kmol/h fresh methanol is needed to maintain the same *p*-xylene production.

4.3 The optimal p-xylene production process

The flow diagram for the optimal p-xylene process with methanol conversion of 98.0 % is illustrated in Figure 8. The detailed stream information is given in Table 8. The mixture of methanol and toluene is fed at 442.5 °C and 4.0 bar to reactor R-101. Methanol is almost completely converted in reactor R-101 compared to the base case. Trace amount of methanol in the bottom of the flash tank is fed to decanter D-101. Since methanol does not appear in the water-rich phase, methanol recovery system is not required. In addition, the flow rate of recycle stream S-18 is 512.0 kmol/h and the toluene fresh feed is set at 215.0 kmol/h (i.e., recycle-to-feed ratio = 2.38) to maintain a quantitative yield of *p*-xylene. The rest of the process in Figure 8 is the same as the base case in Figure 4. Eventually, a flow rate of 179.0 kmol/h *p*-xylene product with a purity of 99.7 wt % is obtained. In addition, in the benzene distillation column (T-101), less than 0.06 % of toluene is found in the top liquid product without recovery, whilst it is more than 1.18 % in Figure 4 (the existing process[15]). The reason is not because of improper design of the distillation column in Ashraf et al.[15], but because the conversion rate of toluene in the *p*-xylene reactor of the existing process is lower than the optimal process resulting in a larger load of toluene in distillation process.

PLEASE INSERT TABLE 8 HERE

Table 8 Stream data for p-xylene production from the optimized process

Stream		S-1	S-2	S-7	S-8	GAS-1	S-12	GAS-2
mole flow	kmol/h	215.24	393.00	1132.74	1226.93	96.87	750.58	8.61
mass flow	kg/h	19832.30	12592.60	80633.10	80633.10	2728.20	70932.70	252.59
vapor fraction		0.00	0.00	1.00	1.00	1.00	0.00	0.00
temperature	˚C	25.00	25.00	240.00	442.50	25.00	21.00	42.44
pressure	bar	1.00	1.00	4.00	4.00	1.10	8.20	8.00
Component Mole Flow								
Toluene	kmol/h	215.24	0.00	727.29	515.56	1.82	513.69	0.00
Methanol	kmol/h	0.00	393.00	393.00	8.40	0.12	2.09	0.09
p-X	kmol/h	0.00	0.00	1.90	189.58	0.23	189.34	0.00
Water	kmol/h	0.00	0.00	0.00	384.60	13.50	2.23	0.15
Benzene	kmol/h	0.00	0.00	10.49	18.24	0.20	18.03	0.24
GH	kmol/h	0.00	0.00	0.00	94.19	80.97	8.84	8.13
m-X	kmol/h	0.00	0.00	0.06	8.21	0.01	8.20	0.00
o-X	kmol/h	0.00	0.00	0.01	8.16	0.01	8.15	0.00
TBB	kmol/h	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
TBMX	kmol/h	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Stream name		S-14	S-17	S-19	S	W	B	PX
mole flow	kmol/h	750.6	205.08	524.50	6.00	23.57	8.50	179.00
mass flow	kg/h	70932.7	21753.30	48208.20	914.54	2951.12	716.70	19003.00
vapor fraction		0.00	0.00	1.00	0.00	1.00	0.00	0.00
temperature	˚C	21.09	184.25	240.00	150.00	156.19	59.00	109.05
pressure	bar	8.20	3.00	4.00	1.50	1.06	0.40	0.43
Component Mole Flow								
Toluene	kmol/h	513.59	1.35	512.05	0.00	0.00	1.28	0.07
Methanol	kmol/h	2.09	0.00	0.00	0.00	0.00	0.00	0.00
p-X	kmol/h	189.34	187.44	1.90	0.00	7.84	1.24	178.37
Water	kmol/h	2.23	0.00	0.00	0.00	0.00	0.00	0.00
Benzene	kmol/h	18.03	0.00	10.48	0.00	0.00	5.98	0.00
GH	kmol/h	8.84	0.00	0.00	0.00	0.00	0.00	0.00
m-X	kmol/h	8.20	8.14	0.06	0.10	0.15	0.00	0.02
o-X	kmol/h	8.15	8.14	0.01	0.00	7.60	0.00	0.50
TBB	kmol/h	0.00	0.00	0.00	4.00	0.01	0.00	0.00
DTBB	kmol/h	0.00	0.00	0.00	2.00	0.01	0.00	0.00
TBMX	kmol/h	0.00	0.00	0.00	0.00	7.97	0.00	0.00

PLEASE INSERT FIGURE 8 HERE

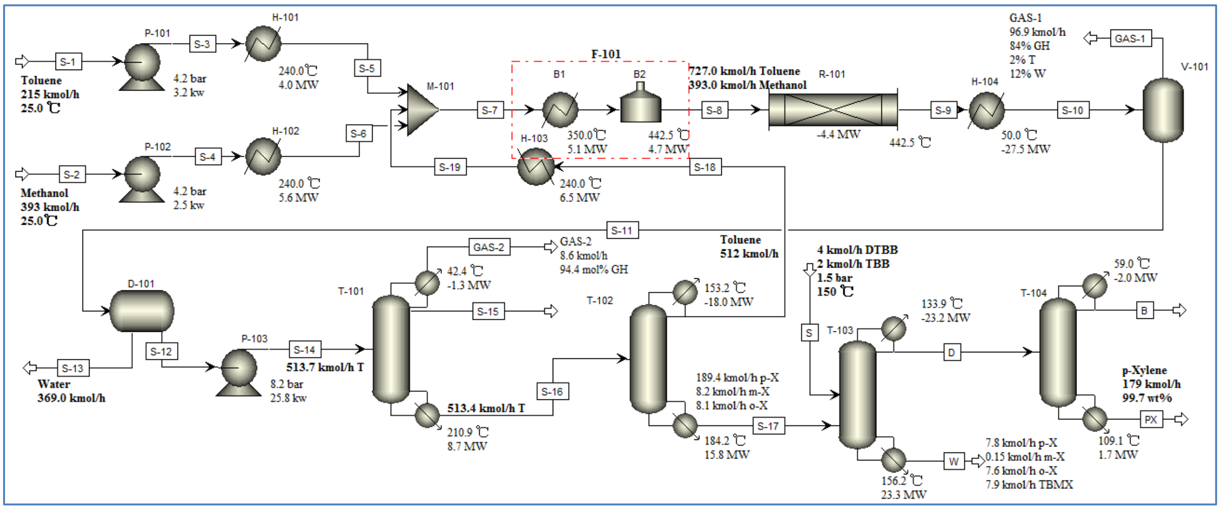

Figure 8 Process flow diagram for the proposed p-xylene production with almost complete methanol conversion

The detailed economic evaluation results for the proposed *p*-xylene production process in Figure 8 are provided in Table 9.

PLEASE INSERT TABLE 9 HERE

Table 9 Economic evaluation results for the proposed *p*-xylene production process

equipment	comments	value	IC (k$)	OC (k$/year)
P-101	toluene pump	3.2	43.9	2.1
P-102	methanol pump	2.5	42.8	1.7
P-103	feed pump	25.8	57.4	18.4
H-101 (MW)	heater	4.0	200.7	1120.7
H-102 (MW)	heater	5.6	215.1	1577.5
H-103 (MW)	heater	6.5	371.6	1831.0
H-104 (MW)	condenser	27.5	361.8	78.5
F-101 (MW)	fired furnace	9.7	1432.9	2825.6
R-101 (MW)	alkylation reactor	4.4	421.2	12.5
V-101	flash vessel	-	173.3	-
D-101	decanter	-	173.0	-
T-101 ([a]C/R, MW)	benzene distillation column	1.3/8.7	1381.5	2431.0
T-102 ([a]C/R, MW)	toluene distillation column	18.0/15.8	2044.4	4483.1
T-103 ([a]C/R, MW)	reaction distillation column	23.2/23.3	4981.5	5300.5
T-104 ([a]C/R, MW)	p-xylene distillation column	1.7/1.4	1112.7	386.2
total cost	-	-	13013.8	20068.8

[a] C represents Condenser and R represents Reboiler

Similarly, in Table 9, we also can find that there is such a significant difference between the condenser and reboiler duties of the benzene distillation column (T-101), the main reason for this is the same as the benzene distillation column (T-102) in section 4.1. In addition, we also compare the economics of the proposed *p*-xylene production process with the base case (i.e., existing process[15]). The main results about heaters and distillation columns are presented in Table 10. The total capital cost (TCI) and total operating cost (TOC) are significantly reduced by 17.3 % and 21.8 %, respectively compared to those of the base case. This is mainly because of the removal of methanol recovery and recycles system, and the reduction of toluene recycle amount.

PLEASE INSERT TABLE 10 HERE

Table 10 Comparative results for the base case and the proposed process

type	base case (the existing process [15])		the proposed process	
	TCI (k$)	TOC (k$/year)	TCI (k$)	TOC (k$/year)
pumps	223.1	30.8	144.1	22.2
heaters	2473.9	9027.0	2582.1	7433.3
distillation columns	12448.0	16591.9	9520.1	12600.8
other units	586.3	11.7	767.5	12.5
total	15731.3	204687.2	13013.8	19094.6
savings (%)			17.3	21.8

4.4 Heat Integration

As seen from Figure 8, the reactor outlet flow in the proposed process (see Figure 8) can provide 27.5 MW of energy without effective utilization. To improve energy efficiency of the proposed process and reduce the operating cost further, heat integration is conducted using Aspen Energy Analysis[40,41], which is based on pinch analysis method. The heat exchanger network (HEN) is automatically created based on the pinch analysis using Aspen Energy

Analysis.[42-44] The minimum temperature approach, ΔT_{min} is assumed to be 10.0 °C.

4.4.1 HEN for the proposed process. The data on hot and cold streams in the proposed process are listed in Table 11. The composite curve of cold and hot streams in the proposed process is shown in Figure 9.

PLEASE INSERT FIGURE 9 HERE

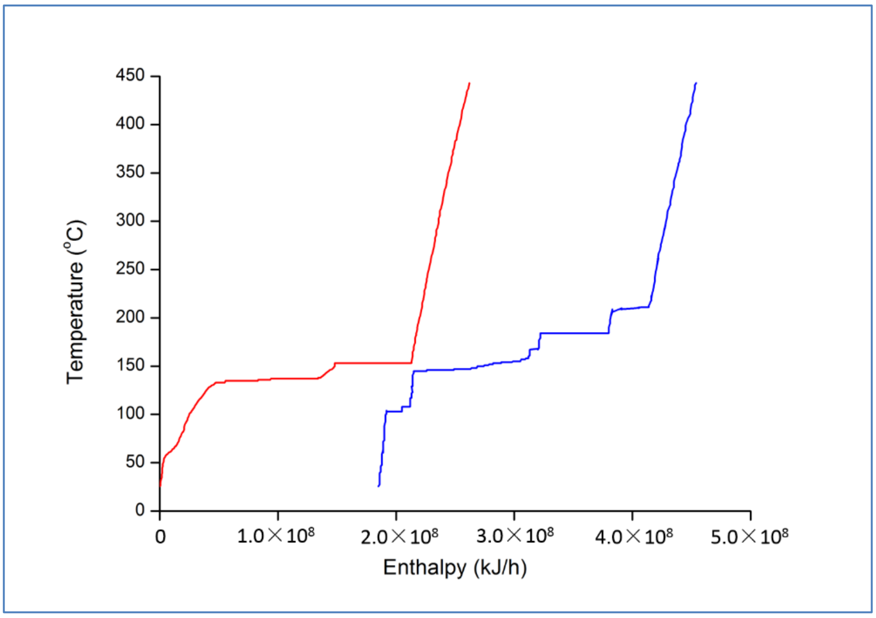

Figure 9 The composite curve of cold and hot logistics in the proposed process

PLEASE INSERT TABLE 11 HERE

Table 11 Thermodynamic data of hot and cold streams in the proposed process

stream	inlet temperature, °C	outlet temperature, °C	heat duty, kJ/h	MCp, kJ/°C h
S-9_To_S-10	442.5	50.0	9.917×10^{7}	4.123×10^{5}
S-3_To_S-5	25.0	240.0	1.440×10^{7}	2.882×10^{7}
S-4_To_S-6	25.0	240.0	2.026×10^{7}	9.078×10^{7}
S-18_To_S-19	153.2	240.0	2.352×10^{7}	1.190×10^{6}
S-7_To_S-8	240.0	442.5	3.533×10^{7}	1.749×10^{5}
V-101_heat	50.0	25.0	3.522×10^{6}	1.409×10^{5}
To Condenser@T-101_TO_GAS-2	147.2	42.4	4.588×10^{6}	8.737×10^{4}
To Reboiler@T-101_TO_S-16	209.0	210.9	3.118×10^{7}	1.614×10^{7}
To Condenser@T-102_TO_S-18	153.7	153.2	6.476×10^{7}	1.310×10^{8}
To Reboiler@T-102_TO_S-17	184.0	184.2	5.692×10^{7}	3.040×10^{8}
To Condenser@T-103_TO_D	137.0	133.9	8.268×10^{7}	4.246×10^{7}

To Reboiler@T-103_TO_W	145.7	156.2	8.041×10^{7}	1.150×10^{7}
To Condenser@T-104_TO_B	73.7	59.0	7.236×10^{6}	5.789×10^{5}
To Reboiler@T-104_TO_PX	108.9	109.1	6.174×10^{6}	7.391×10^{7}

PLEASE INSERT FIGURE 10 HERE

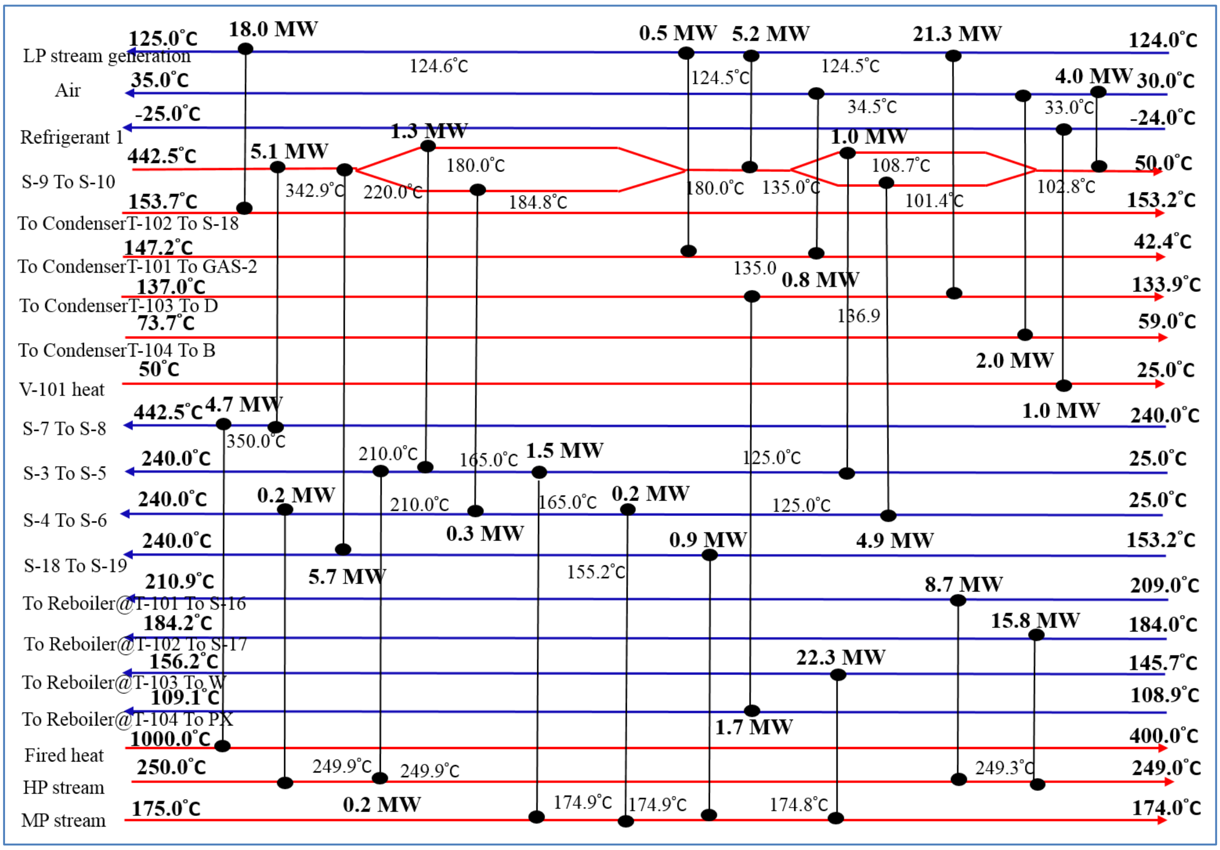

Figure 10 The HEN diagram from the proposed *p*-xylene production process after heat integration

The HEN diagram from the proposed *p*-xylene production process is illustrated in Figure 10. As shown in Figure 10, the reactor effluent (i.e., S9) is first used to preheat the inlet stream (S-7) of the combustion furnace from 240 °C to 350.0 °C, resulting in significant energy reduction in the furnace from 9.7 MW to 4.7 MW. The surplus low-temperature heat is then used to provide energy for fresh and recycle streams (S-3, S-4, and S-18) and produce LP steam. As shown in the figure, the remaining heat energy in this stream (S-9) first supplies energy to the recycle stream because the recycle stream requires a relatively large number of heat and then partially heats up the fresh stream. The thermal coupling of coolers with the reboilers in *p*-xylene separation process also could reduce the energy consumption. The top vapor from T-103 (S-D) is used to provide energy for the reboiler of T-104 (S-PX). After heat integration, the operating cost is decreased by 3123.9 k$/year compared to that in Figure 8 without heat integration.

4.4.2 HEN for the base case. To fairly compare with the base case, we also conduct heat integration for the base in Figure 4. The hot and cold streams for the base case are given in Table 12. The composite curve is illustrated in Figure 11.

PLEASE INSERT FIGURE 11 HERE

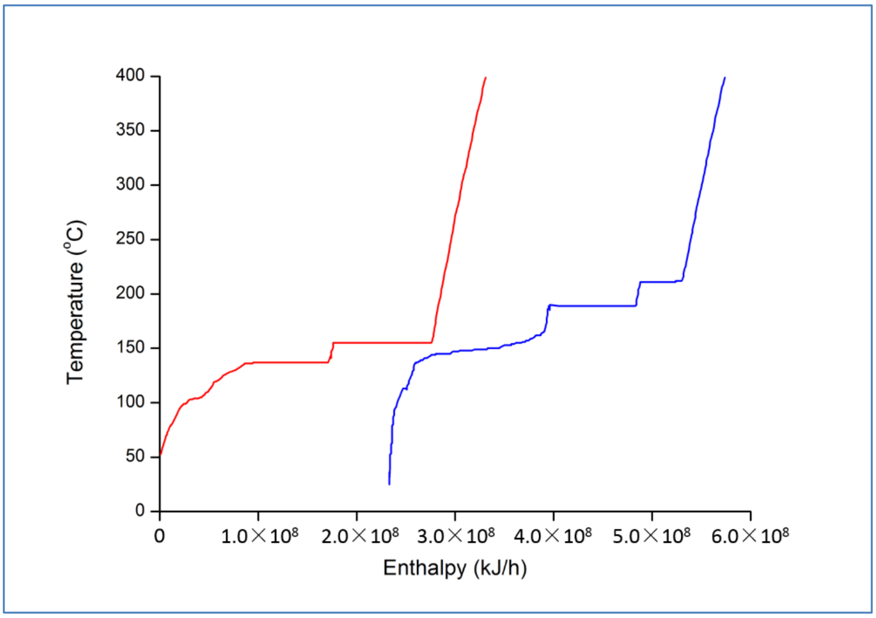

Figure 11 The composite curve of cold and hot logistics in the existing process

PLEASE INSERT TABLE 12 HERE

Table 12 Thermodynamic data for hot and cold streams in the existing process

stream	inlet temperature ˚C	outlet temperature ˚C	heat duty, kJ/h	MCp, kJ/˚C h
S-9_To_S-10	400.0	50.0	1.245×10^{8}	6.409×10^{5}
S-22_To_S-23	136.1	240.0	4.157×10^{7}	1.804×10^{6}
S-3_To_S-5	25.0	240.0	1.444×10^{7}	2.112×10^{5}

S-4_To_S-6	25.0	240.0	2.016×10^{7}	4.840×10^{5}
S-7_To_S-8	240.0	400.0	3.733×10^{7}	2.337×10^{5}
To Condenser@T-101_TO_GAS-2	105.8	70.8	1.211×10^{7}	1.955×10^{6}
To Reboiler@T-101_TO_S-17	145.8	145.9	1.437×10^{7}	2.376×10^{8}
To Condenser@T-102_TO_GAS-3	142.8	74.2	9.824×10^{6}	2.880×10^{5}
To Reboiler@T-102_TO_S-19	211.5	212.7	4.253×10^{7}	3.760×10^{7}
To Condenser@T-103_TO_S-20	156.4	156.0	9.906×10^{7}	2.350×10^{8}
To Reboiler@T-103_TO_S-21	188.8	189.0	8.818×10^{7}	8.000×10^{8}
To Condenser@T-104_TO_D	137.8	136.9	8.168×10^{7}	1.540×10^{8}
To Reboiler@T-104_TO_W	147.4	164.7	7.940×10^{7}	6.576×10^{6}
To Condenser@T-105_TO_B	107.3	92.8	3.315×10^{6}	3.088×10^{5}
To Reboiler@T-105_TO_PX	113.8	113.9	2.345×10^{6}	3.261×10^{7}

PLEASE INSERT FIGURE 12 HERE

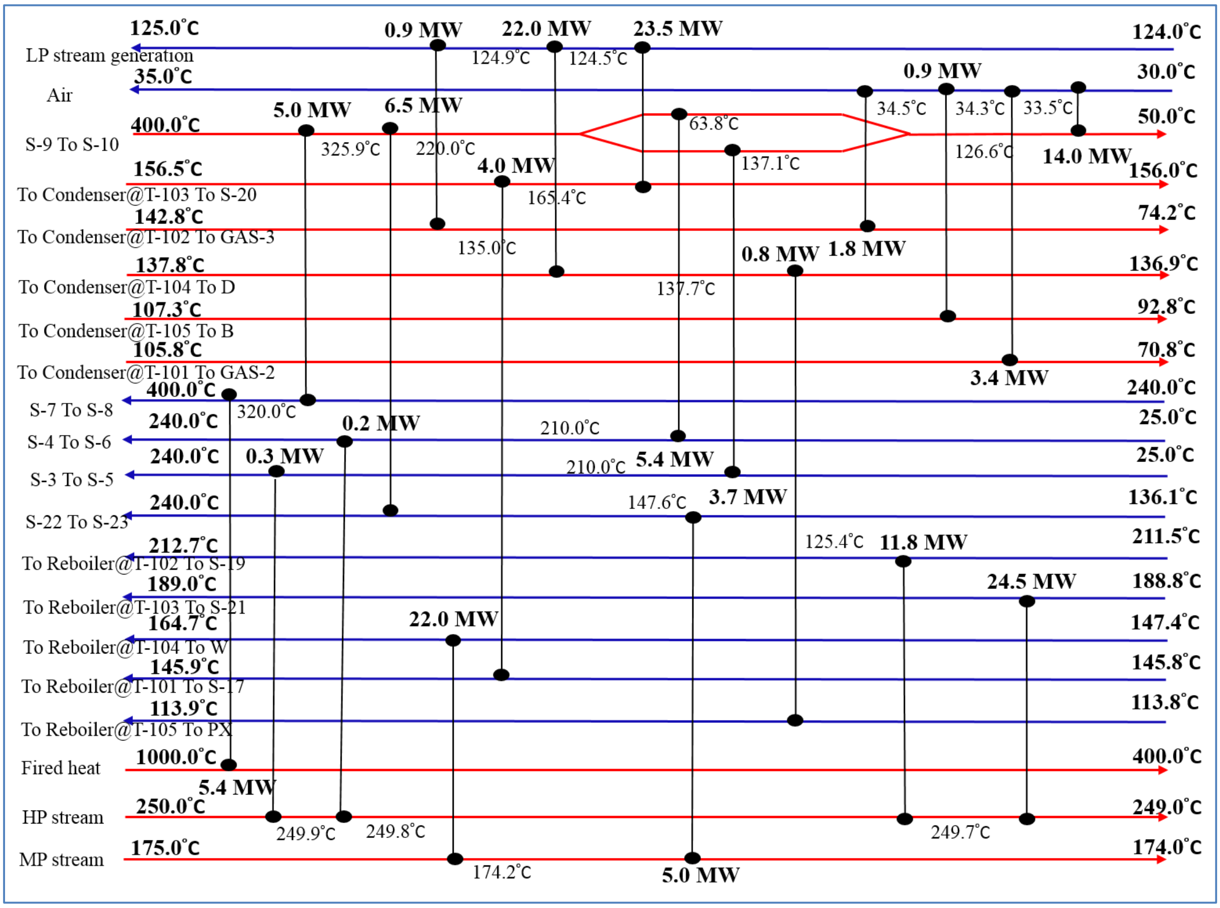

Figure 12 The HEN diagram for the existing *p*-xylene production process

Figure 12 illustrates the HEN diagram from the base case (i.e., the existing *p*-xylene production process). From Figure 12, it can be observed that the reactor effluent is first utilized to heat up the stream (S-7) to the temperature of 320.0 °C before the inlet of the furnace, and reducing the energy consumption of the furnace from 10.4 MW to 5.4 MW. the surplus energy is utilitzed for preheating fresh and recycle streams (S-3，S-4，and S-22). In addition, the top vapor from T-103 and T-104 are utilized to provide energy for the reboilers of T-101 and T-105, respectively. After heat integration, the operating cost is decreased by 1846.5 k$/year compared to the reference process in Figure 4 without heat integration.

4.5 Overall economic and environmental impacts

The overall economic and environmental impacts are summarized in Table 13. The Environmental impact is based on indirect CO_2 emissions, which mainly correspond to electricity and thermal energy consumption in the *p*-xylene production process. Note that the electricity consumption is negligible compared to the thermal energy consumption in the process. The CO_2 emissions associated with thermal energy consumption is assumed to be 8.87×10^{8} ton CO_2/kJ.[35]

As shown in Table 13, the TOC for the proposed process is further reduced by 15.6 % after heat integration, whilst it for the existing process is about 7.2 % after heat integration. The overall total annual cost (TAC) value of the existing process and the proposed process are calculated using eq. 19. The TAC for the proposed process after heat integration is reduced by 4.71 % compared to the existing process without heat integration.

PLEASE INSERT TABLE 13 HERE

Table 13 Comparative results on economic and environmental impacts for the proposed process and the existing process

type	before heat integration		after heat integration		savings
	the existing process	the proposed process	the existing process	the proposed process	
TIC (k$)	15731.3	13013.8	16121.5	12668.2	-
TOC (k$/year)	25661.4	20068.8	23814.9	16945.0	
RMC (k$/year)	175961.0	175961.0	175961.0	175961.0	-
TAC (k$/year)	**206866.2**	200367.7	205149.7	**197128.7**	4.71%
heating duty (kJ/h)	3.404×10^8	2.678×10^8	2.494×10^8	1.964×10^8	-
cooling duty (kJ/h)	3.305×10^8	2.616×10^8	2.396×10^8	1.902×10^8	-
CO_2 emissions ($tCO_2/t_{p\text{-xylene}}$)	**1.54**	1.25	1.15	**0.92**	40.2 %
toluene loss (%)	1.18	0.06	-	-	-

It can be also concluded that significant reduction of CO2 emissions is achieved using the proposed process, which is 40.2% less than that using the existing process. This is mainly because of the removal of the methanol recovery column, decreasing recycled quality of toluene using the proposed *p*-xylene process and heat integration. It should be mentioned that the Toluene loss in the benzene column for the proposed process is much lower than that in the existing process.

5 Conclusions

In this work, an intensified *p*-xylene production process through toluene alkylation was proposed and a systematic design procedure was proposed including thermodynamic and kinetic insight analysis, process simulation, sensitivity analysis, and optimization through Sequential Quadratic Programming tool implemented in Aspen Plus. It was found that the methanol conversion could reach 98.0 % with *p*-xylene selectivity of 92.0 % when the operating temperature reached 442.5 °C, the pressure was about 4 bar and the toluene-to-methanol feed ratio was 1.8. Such *p*-xylene production process led to the removal of methanol recovery column, less toluene loss, and much less recycle toluene in the downstream. After heat integration, the proposed *p*-xylene process could achieve a reduction of 4.71 % in overall TAC and of 40.2% in CO_2 emissions compared to the existing *p*-xylene process without heat integration. The proposed *p*-xylene process provides an alternative way for *p*-xylene production, which is more sustainable. In the future, sensitivity analysis on the effect of the variations in the optimal operating conditions on the process performance will be investigated and efficient process control system will be proposed to guarantee the operating parameters are well controlled to be or close to the set-points when variations in the optimal operating conditions occur.

Acknowledgment

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Supporting Information

The supporting Information is available free of charge via the Internet at http://pubs.acs.org/.

The detailed stream information of the existing process (base case) see in Table S1, these formulas of factor see in Eqs. S1-S4, and the iterative algorithm block diagram of calculating effectiveness diffusion coefficient De see in Figure S1.

Nomenclature

A_i = pre-exponential factor, mol/(g·h·atm^2) or mol/(g·h·atm)

k_i = rate constant, mol/(g·h·atm^2) or mol/(g·h·atm)

E_i = activation energy, kJ/mol

De= effectiveness diffusion coefficient, m^2/s

p = pressure, atm

K_i^R = equilibrium constant, −

wt = mass percent, %

S_p = *p*-xylene selectivity, %

F_T = toluene molar flow rate, kmol/h

F_M = methanol molar flow rate, kmol/h

$F_{p\text{-}X}$ = *p*-xylene molar flow rate, kmol/h

$F_{m\text{-}X}$ = *m*-xylene molar flow rate, kmol/h

$F_{o\text{-}X}$ = *o*-xylene molar flow rate, kmol/h

W = catalyst weight, kg

Subscripts

i = reaction number

T = toluene

M = methanol

m-X = *m*-xylene

o-X = *o*-xylene

p-X = *p*-xylene

Compounds

B = benzene

DTBB = di-*tert*-butyl-benzene

GH = light gaseous hydrocarbons

TBB = *tert*-butyl-benzene

TBMX = *tert*-butyl *m*-xylene

References

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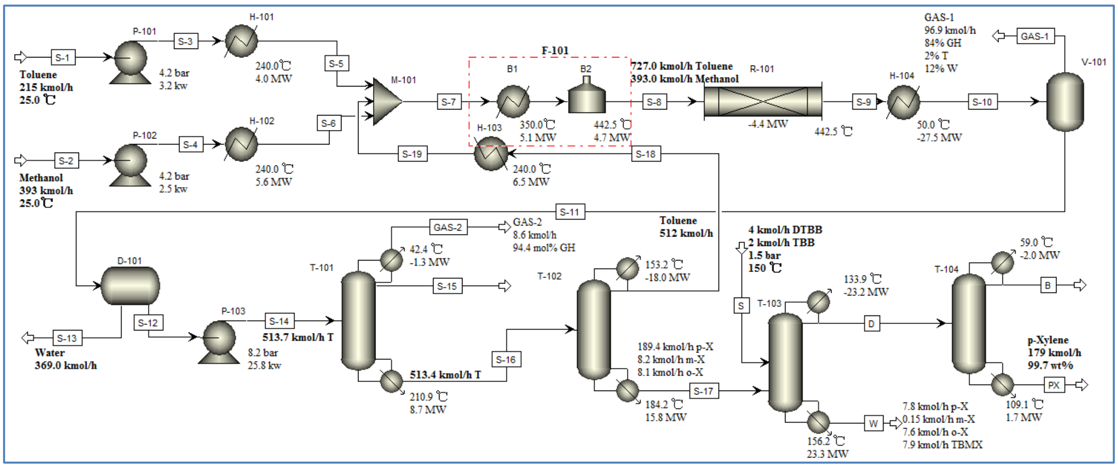
S-1
Toluene
215 kmol/h
25.0 ℃
P-101
4.2 bar
3.2 kw
S-3
H-101
240.0℃
4.0 MW
S-5
S-2
Methanol
393 kmol/h
25.0℃
P-102
4.2 bar
2.5 kw
S-4
H-102
240.0 ℃
5.6 MW
S-6
M-101
S-7
F-101
B1
350.0℃
5.1 MW
B2
442.5 ℃
4.7 MW
H-103
240.0 ℃
6.5 MW
S-19
S-18
727.0 kmol/h Toluene
393.0 kmol/h Methanol
S-8
R-101
-4.4 MW
442.5 ℃
S-9
H-104
50.0 ℃
-27.5 MW
S-10
GAS-1
96.9 kmol/h
84% GH
2% T
12% W
GAS-1
V-101
S-11
D-101
S-13
Water
369.0 kmol/h
S-12
P-103
8.2 bar
25.8 kw
S-14
513.7 kmol/h T
T-101
GAS-2
GAS-2
8.6 kmol/h
94.4 mol% GH
42.4 ℃
-1.3 MW
S-15
210.9 ℃
8.7 MW
513.4 kmol/h T
S-16
T-102
153.2 ℃
-18.0 MW
Toluene
512 kmol/h
189.4 kmol/h p-X
8.2 kmol/h m-X
8.1 kmol/h o-X
184.2 ℃
15.8 MW
S-17
4 kmol/h DTBB
2 kmol/h TBB
1.5 bar
150 ℃
S
T-103
133.9 ℃
-23.2 MW
D
156.2 ℃
23.3 MW
W
7.8 kmol/h p-X
0.15 kmol/h m-X
7.6 kmol/h o-X
7.9 kmol/h TBMX
T-104
59.0 ℃
-2.0 MW
B
p-Xylene
179 kmol/h
99.7 wt%
PX
109.1 ℃
1.7 MW