ANALYSIS AND OPTIMIZATION OF p-XYLENE PRODUCTION PROCESS

by

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In the name of Allah, most Gracious, most Merciful. All praise is due to Allah and may His peace and blessings be upon the Prophet (PBUH).

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Abstract

In this study a process is developed for selective production of p-xylene from toluene methylation using reactive distillation for p-xylene separation. Complete process is simulated in Aspen Plus® and reaction parameters are optimized to get 97.5% p-xylene selectivity using built-in optimization tool. Highly selective p-xylene production greatly reduces the separation cost and also reduces the production of less desired xylene isomers. After separation p-xylene product stream purity of 99.7% is achieved. Then a second law analysis is made on the process developed and lost work of different blocks is compared. Heat integration of the process is done using Aspen Energy Analyzer® resulting in 23% reduced total lost work generation.

Search Terms: p-xylene production, toluene methylation, p-xylene selectivity

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Nomenclature

A_i	pre-exponential factor
C	toluene conversion
k_i	rate constant
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_{To}	toluene feed molar flow rate
F_{Mo}	methanol feed molar flow rate
W_{cat}	catalyst weight
K	equilibrium constant
t	temperature,°C
t_o	surrounding temperature,°C
$\dot{H}$	enthalpy flow
$\dot{S}$	entropy flow
$\dot{A}$	availability function
$\dot{W}$	rate of work
$\dot{Q}$	rate of heat transfer
$L\dot{W}$	lost work
ΔT_{min}	minimum approach temperature

Subscripts

i	reaction number
T	toluene
M	methanol
o	feed
cat	catalyst

Compounds

B	benzene
DTBB	ditertiary butyl-benzene
GH	light gaseous hydrocarbons
M	methanol
m-X	m-xylene
o-X	o-xylene
p-X	p-xylene
T	toluene
TBB	tertiary butyl-benzene
TBMX	tertiary butyl m-xylene
W	water

Chapter 1: Introduction

Xylenes are C_8 aromatic hydrocarbons with two methyl groups attached to benzene ring. p-Xylene (p-X) is one of the three isomers of xylene with methyl group attached at para positions of benzene ring. Other isomers are o-xylene (o-X) and m-xylene (m-X) with methyl group attached at ortho and meta positions, respectively.

p-Xylene is industrially more important than other isomers due to its use as raw material for a number of compounds. Figure 1 shows the xylene isomers production and industrial demand. p-Xylene has the highest demand of 80% from total xylenes while only 24% is produced in total xylenes [1].

> p-Xylene is primarily used as a basic raw material in the manufacture of terephthalic acid (TPA), purified terephthalic acid (PTA) and dimethyl-terephthalate (DMT). TPA, PTA and DMT are used to manufacture polyethylene terephthalate (PET) saturated polyester polymer. Polyesters are used to produce fibers and films. PET bottles are widely used for water because of its non-breakage properties as well as carbonated beverages because of good carbon dioxide barrier properties. In addition, they are light-weight, shatter-resistant and possess high tensile strength. [2]

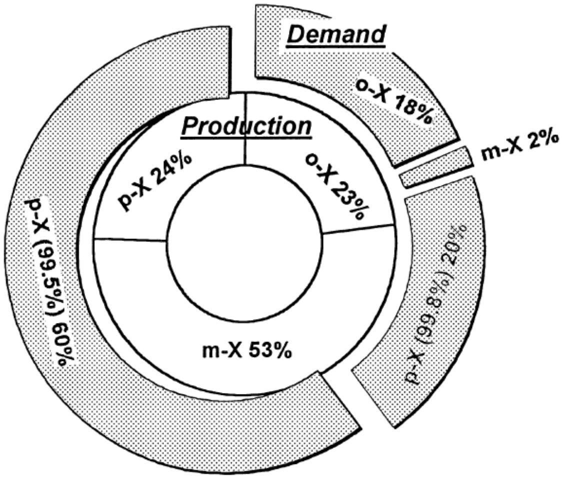


Figure 1. Spectrum of worldwide production rate and market requirements of xylenes [1].

1.1. Market Analysis of p-Xylene

p-Xylene market demand has increased over the years. New capacity has been coming on-stream but it has not matched the steadily increasing demand [3]. Because of high downstream demand, p-xylene generally has 6-8% yearly demand growth [3]. This trend is shown in Figure 2. From 2012 there is a serious concern over p-xylene supply due to recent purified terephthalic acid (PTA) and polyester capacity development [4].

Another factor for increase in demand is the price of cotton. Global cotton fiber production keeps fluctuating and declined by almost 20% from 2004 to 2009. This decline is equivalent to a drop of almost 5 million tons [4]. Due to this decline polyester fiber gained its share in global fiber supply passing 50% in 2011, resulting in increased p-xylene demand. Market for polyester fiber is now substantially larger than that of cotton [4]. As p-xylene is used to make polyester so p-xylene market will remain subject to variations in cotton supply.

Since most plants are already operating at full capacity, further increases may require some type of modification. Existing producers can capitalize in this environment by maximizing production of p-xylene by converting less important compounds, like toluene, to p-xylene.

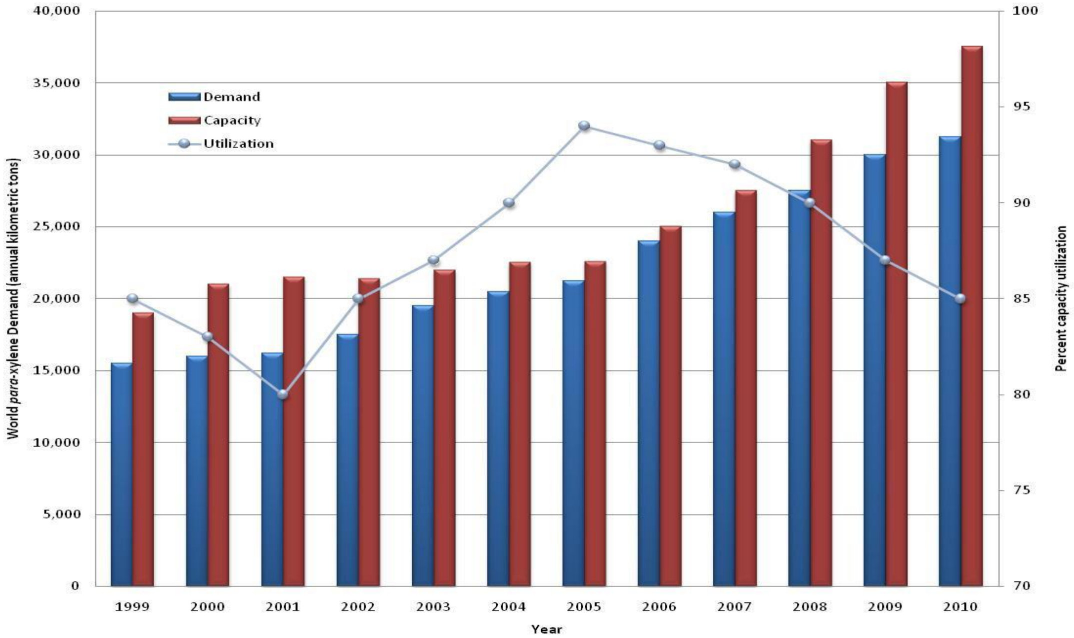


Figure 2. p-Xylene supply and demand balance, 1999-2010 [3].

1.2. Production Method of p-Xylene

Industrially most of p-xylene is produced by catalytic reforming of naphtha [5]. Xylene isomers are produced along with other aromatics, like benzene and toluene, from catalytic reforming of naphtha. Other methods include conversion of toluene, like toluene disproportionation and toluene methylation with methanol. Toluene has the lowest demand as compared to benzene and xylenes and there is a strong incentive to convert surplus toluene to more valuable aromatics [1]. Figure 3 shows the comparison of worldwide BTX (benzene, toluene, and xylenes) distribution patterns of production and market demand. Toluene has only 11% demand in total BTX and it can be converted to more important aromatics like p-xylene by toluene disproportionation or toluene methylation.

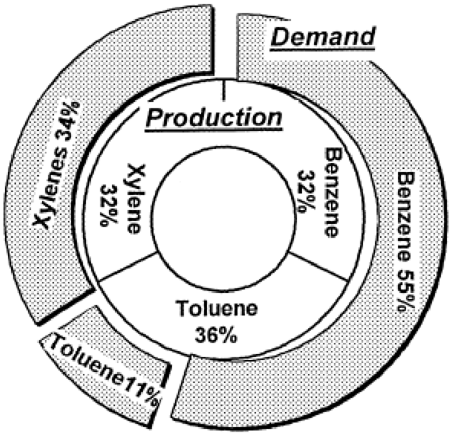


Figure 3. Comparison of worldwide BTX distribution patterns of production and market demand [1].

1.2.1. Catalytic reforming of naphtha.

Major source of p-xylene and other aromatics, BTX, these days is catalytic reforming of naphtha and to some extent by products of steam cracking of naphtha [5]. But these methods produce a dilute mixture of p-xylene with other unimportant isomers, m-xylene and o-xylene, along with ethyl benzene (EB) [5]. Table 1 shows naphtha distribution and worldwide demand of xylene isomers.

Due to shortcoming of these methods to produce high purity p-xylene, purification is required to separate p-xylene from these compounds, which have very close boiling points. To increase the volume production the unimportant isomers o-xylene and m-xylene are converted to p-xylene by isomerization. Consequently the cost of production increases.

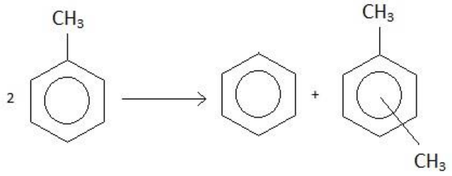
Table 1. Feedstock distribution of xylene isomers compared to worldwide demand [5]

Xylene isomers	ethyl benzene	p-xylene	m-xylene	o-xylene
	Distribution			
Reformed naptha (C_8) cut	18%	21%	41%	20%
Pygas(C_8) cut	52%	12%	25%	11%
Demand for separated isomers	1%	86%	3%	10%

Catalytic reforming of naphtha consists of a reforming and pyrolysis section. BTX aromatics produced are separated from non-aromatic raffinate via extraction [5]. BTX are further separated to get benzene, toluene, and C_8 xylene streams in product recovery section. p-Xylene is usually recovered by either crystallization or adsorption method [1].

1.2.2. Toluene disproportionation.

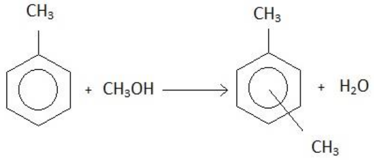
In toluene disproportionation two molecules of toluene react over an acid zeolite catalyst to form one xylene and one benzene molecule [6]. This technology encompasses three main processing areas: reactor section, product distillation and p-xylene recovery. p-Xylene selectivity of 90% in the mixed xylenes is achievable and can be separated by using crystallization or adsorption [7]. This process also produces benzene; therefore it is feasible when benzene is also required along with the xylenes [8].



(1.1)

1.2.3. Methylation of toluene.

Catalytic methylation of toluene is a potential alternative to produce p-xylene if the cost of methanol remains low [9]. By reacting toluene and methanol over a zeolite catalyst, such as ZSM-5, water and xylenes are formed with the following thermodynamic equilibrium composition of xylene isomers; 23.55% p-xylene, 52.42% m-xylene, and 24.03% o-xylene at 400℃ [10].



(1.2)

Due to the very close boiling points of the different xylene isomers, separation of p-xylene from xylene mixtures is difficult and represents an extensive energy step in the whole production process. Also, other isomers do not have much industrial demand and isomerization is needed to convert them to p-xylene which results in additional production cost [1]. 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 [11–14].

Modification of ZSM-5 catalyst has been tried with a number of additives, shown in Table 2 [15]. These experimental results show that p-xylene selectivity higher than 90% is possible with boron and magnesium modification. Although the boron modified ZSM-5 gives selectivity higher than 99.9% the stability of B/ZSM-5 catalysts is an issue due to loss of boron from the catalyst during reaction [15]. Selectivity from Mg modified ZSM-5 can be further enhanced by minimizing the contact time on external acid sites so that undesirable isomerization can be reduced [9]. Kinetics of toluene alkylation in chapter 2 will highlight more about this trend.

Table 2. Toluene methylation reaction on various modified ZSM-5 catalysts (Reaction conditions: flow rates—toluene, 3.2 cm^3/min; methanol, 0.4 cm^3/min; water, 3.6 cm^3/min; hydrogen, 7.2 cm^3/min; nitrogen, 185.6 cm^3/min) [15]

Catalyst description	Toluene conversion (%)	Selectivity (%)		
		p-Xylene	m-Xylene	o-Xylene
HZSM-5	6.4	23.3	51	26
10% B/ZSM-5	5.5	>99.9	0	0
10% P/ZSM-5	0.3	36.7	21.9	30.3
10% Mg/ZSM-5	6.5	92.7	5.9	1.4
10% Fe/ZSM-5	5.7	36.8	43.8	19.5
10% Ga/ZSM-5	3.5	39.6	43.3	17.1
10% Pr/ZSM-5	4.5	51.5	35.1	13.4
10% Tb/ZSM-5	11.2	59.6	29.4	11
10% Sn/ZSM-5	7	42.3	38.7	19
10% Al/ZSM-5	7.4	49.3	37.3	13.4

To increase the p-xylene production, the direct conversion of toluene to p-xylene is a desirable alternative. In our study, a novel process is developed to produce high purity p-xylene that does not require classical xylene separation technologies like crystallization or adsorption. p-Xylene is purified by reactive distillation to meet the product purity specification. Aspen Plus® process simulator is used for the simulation of the proposed process, which utilizes the latest findings related to the catalytic methylation of toluene over Mg modified ZSM-5 zeolite catalyst.

1.3. Purification of p-Xylene

Typically the minimum p-xylene purity required in industry is 99.5% while 99.8% is considered ultrapure [1]. All the methods discussed above require the separation of p-xylene from other isomers. Also before that, it is required to separate xylenes from toluene and the other side products like water, ethylene, and benzene etc. The methods used in the industry for xylene separation are described below. These separation methods differ in capital and operating cost. We anticipate that the best method depends on the purity and flow rate of the stream to be purified.

1.3.1. Crystallization.

Boiling and freezing points data for benzene, toluene and xylenes is shown in Table 3. Due very close boiling points of xylenes it is a challenge to separate p-xylene from its isomers. Benzene can be separated by distillation; however extensive distillation is required to separate o-xylene and m-xylene. m-Xylene and p-xylene cannot be separated by distillation economically. Due to wide range of freezing points, as shown in Table 3, it is possible to separate xylene isomers by lowering the temperature. p-Xylene having the highest freezing point will crystallize first and the solid crystals can be separated by using filtration or centrifugation [16]. Crystallization occurs by cooling the mixture to supersaturation resulting in formation of crystal nuclei and its subsequent growth. Cooling is achieved by using jacketed crystallizer, scraped surface heat exchanger, and direct cooling techniques like injection of miscible or immiscible refrigerant (liquid CO_2) [16]. The crystallization process is more suitable when the stream has low concentration of p-xylene. A typical single pass p-xylene recovery is 60-65 % [17]. Several plants use this method the get purified p-xylene.

Table 3. Physical properties of xylene isomers [18]

	Normal Boiling Point, ℃	Freezing Point, ℃
benzene	80.1	5.5
toluene	110.6	-95.0
p-xylene	138.3	13.2
m-xylene	139.1	-47.9
o-xylene	144.3	-25.2

1.3.2. Adsorption

Second method to separate xylenes is by selective adsorption on molecular sieve. Due to different positions of methyl group xylenes have different kinetic diameters: 6.7 Å for p-xylene, 7.3 Å for o-xylene, and 7.4 Å for m-xylene [19]. This results in relatively high diffusion coefficient of p-xylene than other isomers and selective adsorption of p-xylene is used to separate p-xylene from its isomers.

One such method is Simulated Moving Bed (SMB) technology which recovers p-xylene from mixed xylenes. The industrial SMB units operate in liquid phase (temperature = 180 °C and pressure = 9 bar) and produces high p-xylene purity and recovery. It offers high single pass efficiency, and extended adsorbent life [17]. Typical p-xylene recovery per pass is over 95% for simulated moving bed technology, compared to only 60-65% for crystallization [17]. Separation is accomplished by exploiting the differences in affinity of the adsorbent for p-xylene relative to the other C_8-isomers on faujasite-type zeolites, among which prehydrated KY, BaKX and BaX zeolite hold an important place [17]. 99.9% pure p-xylene is recovered in the extract while a mixture of o-xylene and m-xylene is withdrawn in the raffinate [17].

1.3.3. Distillation

Benzene/toluene and o-xylene/p-xylene have relative volatility of 3.09 and 1.17 respectively. Benzene can be separated from the mixture by distillation quite easily while o-xylene separation requires extensive distillation due to low relative volatility. Separation of p-xylene and m-xylene is very difficult by ordinary distillation due to close boiling points giving very low relative volatility of 1.02. Due similar molecular structure they are not influenced by presence of third component and extractive distillation does not work.

p-Xylene and m-xylene can be separated by reactive distillation as reported by Saito et al. [20]. This method involves alkylating the mixture of xylenes. m-Xylene reacts preferentially with di-tertiary butyl-benzene (DTBB) and tertiary butyl-benzene (TBB) to form tertiary butyl m-xylene (TBMX) and benzene (B). The reactions are shown in equations 1.1 and 1.2 [20]. m-Xylene forms higher boiling tertiary butyl m-xylene and can be separated from p-xylene by fractionation easily. Table 4 shows the normal boiling points of DTBB, TBB, and TBMX.

$$DTBB + m\text{-}X \rightleftharpoons TBMX + TBB \tag{1.1}$$

$$TBB + m\text{-}X \rightleftharpoons TBMX + B \tag{1.2}$$

Table 4. Normal boiling points of DTBB, TBB, and TBMX [20]

Component	Normal Boiling Point, ℃
DTBB	230
TBB	169.3
TBMX	205

The reactions takes place rapidly and attains equilibrium immediately [21, 22]. Benzene produced in the alkylation reaction is the lightest and is distilled off which results in disturbing the equilibrium. Equilibrium data is given by Saito et al. [20] and shown in equations (1.3) and (1.4) for the reactions in equations (1.1) and (1.2), respectively.

$$K^R = \frac{x_{TBMX}\, x_{TBB}}{x_{DTBB}\, x_{m-X}} = 0.6 \tag{1.3}$$

$$K^R = \frac{x_{TBMX}\, x_{B}}{x_{TBB}\, x_{m-X}} = 0.16 \tag{1.4}$$

Chapter 2: Toluene Methylation

As mentioned in section 1.2.3 the toluene methylation on ZSM-5 catalyst produces a mixture of xylenes with only 23% p-xylene. Studies have shown that modification of the zeolite catalysts results in high p-xylene selectivity [11–14]. The selectivity of p-xylene can also be increased by optimizing the process variables such as temperature, pressure, contact time and the feed ratio of toluene and methanol. These process variables affect the mechanism of the reaction between toluene and methanol and the isomerization reaction taking place in parallel. Section 2.2. highlights the major steps in the mechanism of this process.

2.1. ZSM-5 Zeolite Catalyst

Due to formation of carbonium ion in toluene methylation reaction the catalyst used are acidic. Initially Friedel and Crafts catalysts were used; these were modified with $AlCl_3$ or HCl [22–24]. However, these catalysts have low p-xylene selectivity and deactivate rapidly. They were replaced by zeolite catalysts which have high catalytic activity, improved resistance towards deactivation, high xylene selectivity and more importantly increased p-xylene selectivity. Different zeolite catalysts were tried in toluene methylation: zeolite 13X, zeolite Y, zeolite Fu-1, zeolite ZSM-5 and zeolite ZSM-8; the most used for toluene methylation is ZSM-5 [25]. ZSM-5 offers superior shape selective properties that are essential in selective production of p-xylene [8]. ZMS-5 offers good thermal stability with temperature limitations of 720-945 °C, depending on Si/Al ratio [26]. Cheng et al. [27] reported that ZSM-5 offers high thermal stability and ZSM-5 has only 5.8% mass loss when heated from room temperature to 800 °C.

ZSM-5 (Zeolite Socony Mobil - 5) is a synthetic aluminosilicate that belongs to pentasil family of zeolites [28]. Its structural unit contains twelve fundamental units (SiO_2 and AlO_4) linked through oxygen, as shown in Figure 4. These structural units join to form chains and these chains then join to make structural planes as shown is Figure 5 and Figure 6, respectively. Structural planes join to make a three dimensional structure of ZSM-5 as shown in Figure 7 [29].

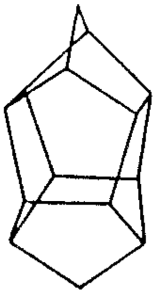


Figure 4. ZSM-5 structural unit [29].

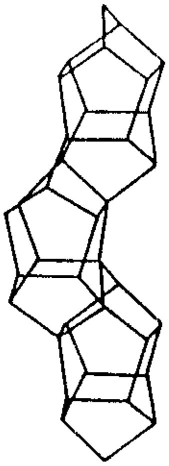


Figure 5. ZSM-5 structural chain [29].

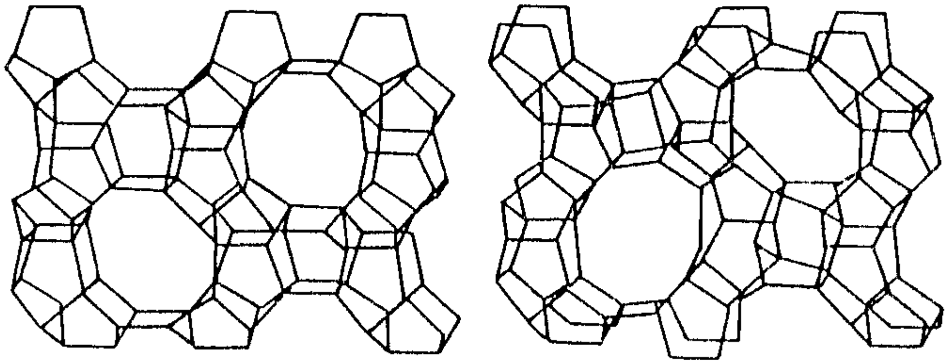


Figure 6. ZSM-5 structural planes [29].

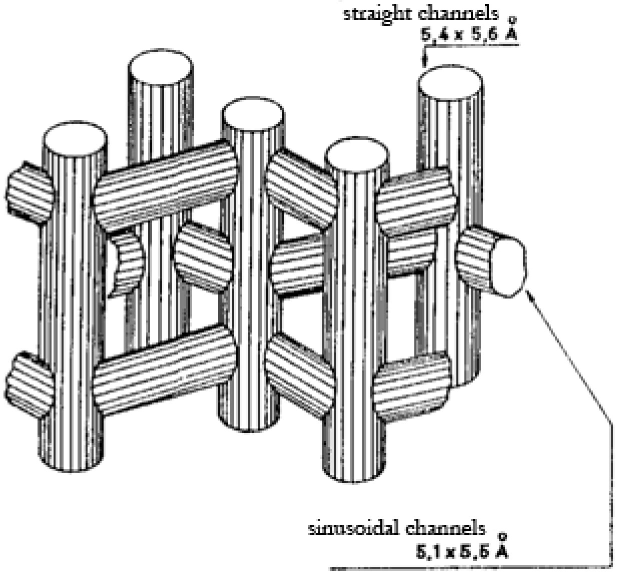


Figure 7. ZSM-5 three dimensional structure and channel system [29].

There are two types of channel systems in ZSM-5 zeolite as shown in Figure 7. One is straight with elliptical cross section (5.7 × 5.1 Å) and parallel to the direction (010). The second one has zigzag pattern with almost circular cross section (5.4 × 5.6 Å) and extends in the direction (001). Csicsery et al. [30] has shown that ZSM-5 has effective diameter in the range 6.9 to 7.2 Å.

The uniformity of pore size and well-defined structure gives this zeolite molecular sieve properties. This allows the diffusion of those molecules which have size less than the effective passage section of the pore. This justifies its use as catalyst in petrochemical processes requiring high selectivity.

2.2. Mechanism of Toluene Methylation over Mg-ZSM-5

Toluene methylation has been investigated over different medium pore size zeolite catalysts. ZSM-5 is mostly used due to its shape selective properties which result in high p-xylene selectivity [10]. It has internal and external acid sites which act as reaction sites. Several papers discussed the mechanism of toluene methylation (equation 2.1) but unfortunately the full details are still not known [31–33]. It is currently accepted that toluene ring alkylation with methanol over zeolites proceeds via chemisorption of methanol on the internal acid sites, followed by formation of surface-active species such as methoxy groups or methoxonium ions, which can further react with weakly adsorbed toluene [34].

$$\textit{Toluene} + \textit{Methanol} \longrightarrow \textit{Xylene} + \textit{Water} \tag{2.1}$$

$$\textit{p-Xylene} \longrightarrow \tfrac{1}{2}\,(\textit{m-Xylene} + \textit{o-Xylene}) \tag{2.2}$$

Following are the steps of toluene methylation reaction [34]

a. diffusion of toluene and methanol inside pores of catalyst
b. adsorption and chemical reaction on active centers
c. desorption and diffusion of products out via isomerization

Equilibrium mixture of xylene is formed inside catalyst pores, 23% p-xylene, 51% m-xylene and 26% o-xylene [10]. Methylation of toluene, in addition to some other side reactions like xylene isomerization, occurs inside the pores of the zeolite catalyst.

The xylene produced inside the pores of the zeolite catalyst has to diffuse out from inside pores to outside. Mirth et al. [35] have reported that diffusion plays an important role in the transport of xylenes from inside of pores to outside where 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 ºC. From equilibrium mixture of xylene formed inside the pores of the catalyst, the relative higher diffusivity of p-xylene as compared to that of o-xylene and m-xylene makes p-xylene the primary product just outside the pores of the catalyst [2]. The p-xylene coming out of the pores isomerizes (equation 2.2) on the external acid sites which reduces the p-xylene selectivity [36]. The controlling parameters for p-xylene selectivity are pore size and external acid sites.

Effect of zeolite medication: The p-xylene selectivity can be increased by zeolite modification which neutralizes the unselective external acid sites and also reduces the effective catalyst pore size [37]. The higher p-xylene selectivity over the modified zeolite, used in Faramawy [38], is attributed to removal of external surface acid sites and smaller pore openings size [38]. Due to high p-xylene diffusivity the concentration of m-xylene and o-xylene increases inside the pores, thus promoting their isomerization to p-xylene and enhancing p-xylene selectivity [15].

Effect of process parameters: Selectivity of p-xylene can be further increased by optimizing the reactor parameter [9], [15]. High space velocity (equivalent to low space time) reduces the contact time at external surface and suppresses the xylene isomerization reaction over the external surface [9]. Breen et al. [9] have reported p-xylene selectivity close to 100% by using Mg modified ZSM-5 catalyst at low space time. Sotelo et al. [39] 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. Low space time can be achieved by adding inert, like N_2 or H_2O, to reaction feed or by using high reaction feed flow rates. High p-xylene selectivity results in negligible production of unwanted xylene isomers and significant reduction in separation cost of p-xylene.

2.3. Kinetics of Toluene Methylation over Mg modified ZSM-5

Kinetic data for toluene methylation over Mg modified ZSM-5 catalyst is reported by Valverde [29]. The characteristics of the Mg modified ZSM-5 catalyst used are described below

- Si/Al ratio : 29
- Magnesium ratio in the catalyst: 1.09 wt%
- Activation:
  - Ion Exchange: HCl 1.0 M, 25 ^{0}C
  - Calcination: 600 ^{o}C, 6 hr
- Agglomeration:
  - Binder: 35 wt% sodium montmorillonite
  - Average particle size: d_p = 0.75 mm

There are five reaction considered by Valverde [29] in finding the kinetics of toluene methylation, including the main and side reactions. The reactions considered are: toluene methylation, methanol dehydration, toluene disproportionation, p-xylene de-alkylation, and p-xylene isomerization. The five reactions involved, together with their observed rate expressions are shown in equations (2.1)-(2.5) [29], respectively. '*k*' denotes rate constant and '*p*' represents partial-pressure. Gaseous hydrocarbons (GH) represent light species (e.g., methane, ethane, ethylene, propane, propene, and the different butanes) which are produced during methanol dehydration and p-xylene dealkylation reactions. GH is used for collectively representing gaseous hydrocarbons in the kinetic study by Valverde [29], in our study it is modeled as pure ethylene because it balances the stoichiometric equations. In p-xylene isomerization reaction, equation (2.7), it is assumed that equal amounts of m-xylene and o-xylene are produced as assumed in Sotelo et al. [39]. Reactions in equations (2.3), (2.5), and (2.6) occur inside pores of the catalyst and effectiveness factor η_1, η_3, and η_4 are used to account for diffusion limitations, respectively [29]. The kinetic parameters found by Valverde [29] are given in Table 5, whereas values of the effectiveness factors, η_3 and η_4, for the catalytic system under consideration are given in Table 6 at three levels of operating temperatures; that is, 460 °C, 500 °C, and 540 °C, respectively. Value of effectiveness factor η_1 is 0.98 and can be assumed equal to 1 [29].

toluene methylation (main reaction):

$$T + M \longrightarrow p\text{-}X + W \qquad r_1 = k_1 p_T p_M \tag{2.3}$$

methanol dehydration:

$$M \longrightarrow \tfrac{1}{2}\, GH + W \qquad r_2 = k_2 p_M^2 \tag{2.4}$$

toluene diproportionation:

$$2\,T \longrightarrow B + p\text{-}X \qquad r_3 = \eta_3 k_3 p_T \tag{2.5}$$

p-xylene dealkylation:

$$p\text{-}X \longrightarrow T + 1/2\, GH \qquad r_4 = \eta_4 k_4 p_{p-X} \tag{2.6}$$

p-xylene isomerization:

$$2\,p\text{-}X \longrightarrow m\text{-}X + o\text{-}X \qquad r_5 = k_5 p_{p-X} \tag{2.7}$$

The reaction rate constants, k_n, are given by equation (2.8) where A_n is the pre-exponential factors and E_n is the activation energy, and *n (1-5)* is the reaction number.

$$k_n = A_n exp^{\frac{-E_n}{RT}} \qquad n = 1 - 5 \tag{2.8}$$

Table 5. Kinetic data of toluene methylation over Mg-ZSM-5 catalyst [29]

Parameter	**Pre-exponential Factor**	**E_n (kJ/mol)**
k_1	403 ± 5 mol/g.h.atm^2	45.7 ± 0.4
k_2	1346 ± 64 mol/g.h.atm^2	50.6 ± 0.5
k_3	96.2 ± 1 mol/g.h.atm	59.0 ± 0.5
k_4	0.3815 ± 0.05 mol/g.h.atm	19.6 ± 0.7
k_5	46.94 ± 0.5 mol/g.h.atm	48.9 ± 0.3

Table 6. Kinetic data of toluene methylation over Mg-ZSM-5 catalyst: effectiveness factors [29]

Temperature ^{o}C	$\boldsymbol{\eta_3}$	$\boldsymbol{\eta_4}$
460	0.7781 ± 0.117	2.977 ± 1.10
500	0.5335 ± 0.170	3.212 ± 0.59
540	0.4470 ± 0.320	3.201 ± 0.97

Chapter 3: Reactor Modeling and Optimization

By using the toluene methylation kinetic data, reported by Valverde [29], an isothermal packed bed reactor is modeled in Aspen Plus®, as shown in Figure 8. The reactions occur in a packed bed reactor with all the reactants fed in gas phase. Aspen Plus® plug flow reactor block is used for this purpose with Peng-Robinson property method. The catalyst bed void fraction used is 0.35. Packed bed reactor model results are compared with the published experimental data in Sotelo et al. [39]. Then the effects of process variables on p-xylene selectivity and conversion of toluene is analyzed by using the sensitivity analysis tool available in Aspen Plus® [40].

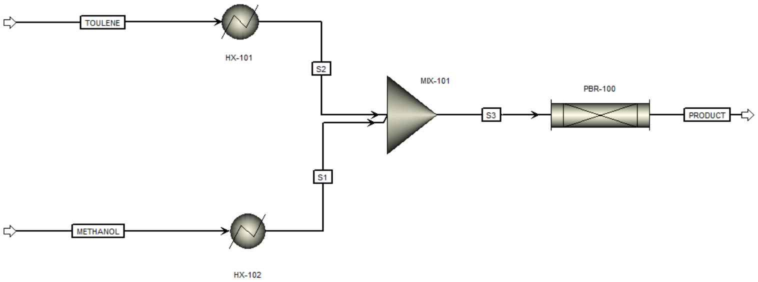


Figure 8. Isothermal reactor simulation PFD.

3.1. Comparison of Model Results with Published Experimental Data

Kinetic data of toluene methylation process is given in section 2.3. This data is used in packed reactor model of Aspen Plus®. Results of the simulation are compared with the experimental data reported in Figures 6 and 7 in Sotelo et al. [39] and are shown in Figure 9 and 10, respectively.

The simulation results are in good agreement with the experimental data reported by Sotelo et al. [39]. Figure 9 shows the comparison between present model (—460℃, ---500℃) and experimental data (● 460℃, ■ 500℃) of toluene and p-xylene mole fraction, in the reactor outlet, at varying space time (weight of catalyst per unit feed flow rate of toluene, W_{cat}/F_{To}) and at two temperature levels, 460℃ and 500℃. Figure 10 shows the comparison between present model (—460℃, ---500℃) and experimental data (● 460℃,

■ 500℃) of toluene and p-xylene mole fraction, in the reactor outlet, at varying toluene-to-methanol feed ratio, F_{To}/F_{Mo}, at two temperature levels, 460℃ and 500℃.

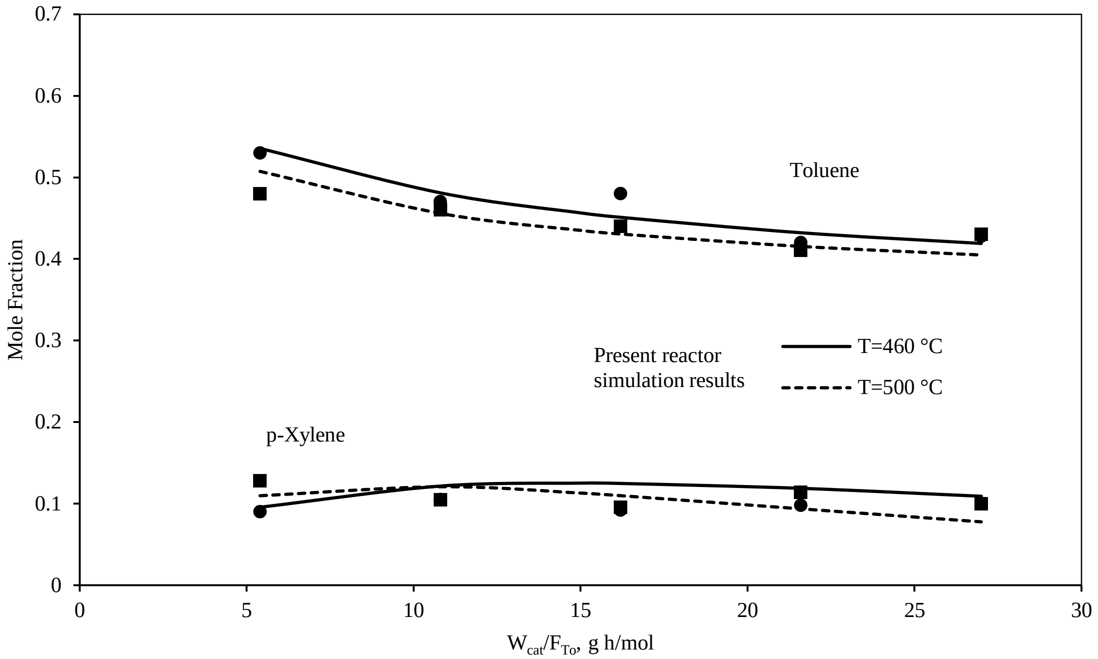


Figure 9. Comparison between experimental data reported in Figure 6 in Sotelo et al. [39] **(● 460℃, ■ 500℃) and present reactor simulation results (F_{To}/F_{Mo} = 2).**

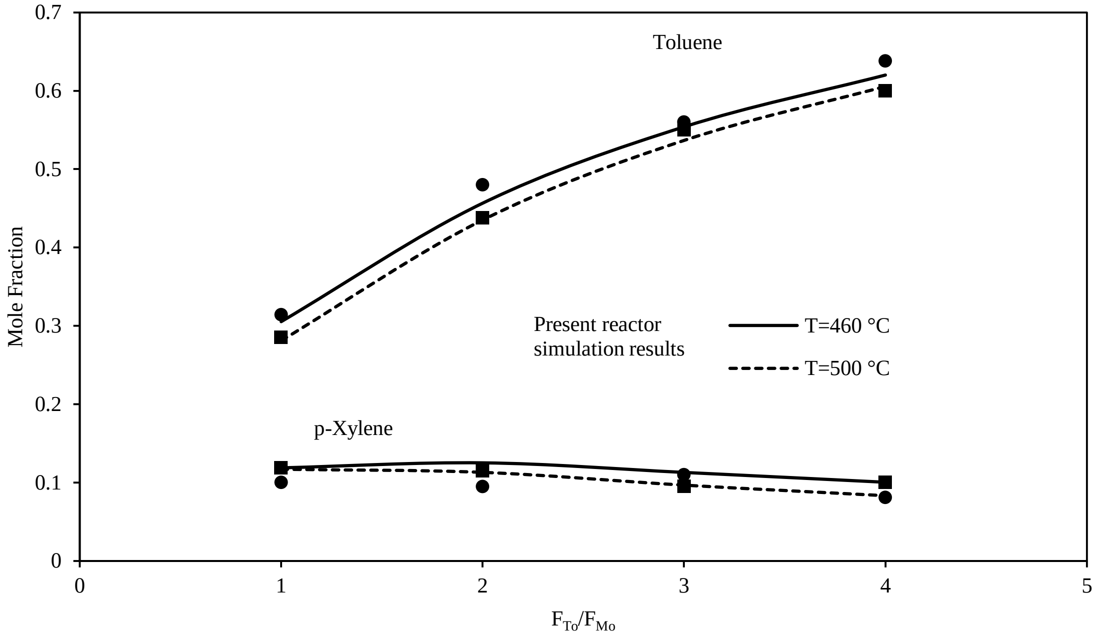


Figure 10. Comparison between experimental data reported in Figure 7 in Sotelo et al. [39] **(● 460℃, ■ 500℃) and present reactor simulation results (W_{cat}/F_{To} = 15 g h/mol).**

3.2. Effect of Process Variables

The effect of process variables (temperature, toluene-to-methanol feed ratio, pressure, space time and water in the feed) on the conversion of toluene and p-xylene selectivity is analyzed. Before that some of the terms are defined for this analysis.

Conversion**:**

$$C = \frac{moles\ of\ toluene\ reacted}{moles\ of\ toluene\ fed\ to\ the\ reactor} \times 100 \tag{3.1}$$

Selectivity of total xylenes:

$$S_X = \frac{moles\ of\ xylenes\ formed}{moles\ of\ toluene\ reacted} \times 100 \tag{3.2}$$

Selectivity of p-xylene:

$$S_P = \frac{moles\ of\ para\!-\!xylene\ formed}{moles\ of\ xylene\ formed} \times 100 \tag{3.3}$$

3.2.1. Effect of Temperature

The effect of temperature on the toluene conversion *C*, total xylene selectivity S_X, and p-xylene selectivity S_p is analyzed by using sensitivity analysis tool. The analysis is made at toluene-to-methanol feed ratio, F_{To}/F_{Mo}, of 1 and at space time, W_{cat}/F_{To}, value of 15 g h/mol. The results are shown in Figure 11.

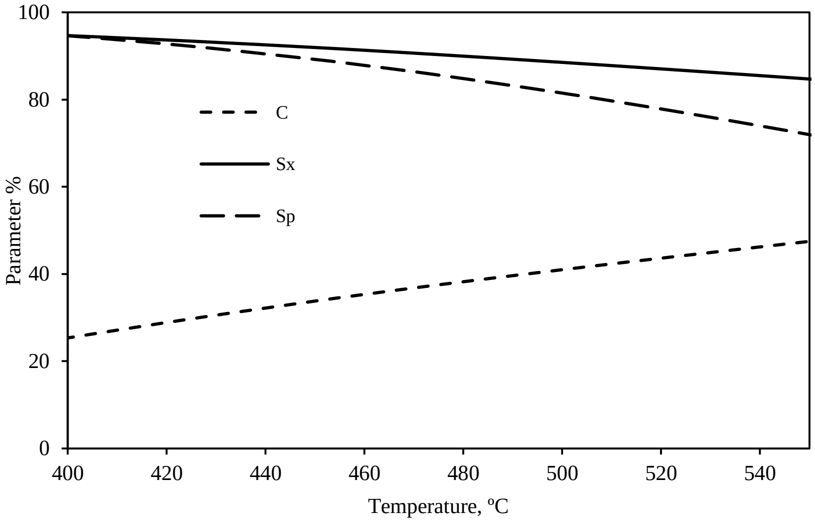


Figure 11. Effect of temperature on conversion, selectivity of total xylenes, and selectivity of p-xylenes (F_{To}/F_{Mo} = 1, W_{cat}/F_{To} = 15 g h/mol, pressure = 1 bar).

We can see from the temperature change trend that by increase in temperature conversion *C* increases. However by increase in temperature the xylene selectivity S_X decreases and p-xylene selectivity S_p decreases more sharply. So there is tradeoff between conversion and selectivity with increase in reactor temperature.

3.2.2. Effect of Toluene-to-Methanol Feed Ratio

Feed ratio of the reactants, F_{To}/F_{Mo}, to reactor is an important process variable which can affect the conversion and selectivity and also the undesired side reactions, such as methanol dehydration reaction.

The results of this analysis are shown in Figure 12. It is clear that conversion and selectivity both decrease with increase in toluene-to-methanol feed ratio. So, it is not advantageous to feed extra toluene in the reactor. For toluene-to-methanol feed ratio of less than 1 effect on conversion is not significant.

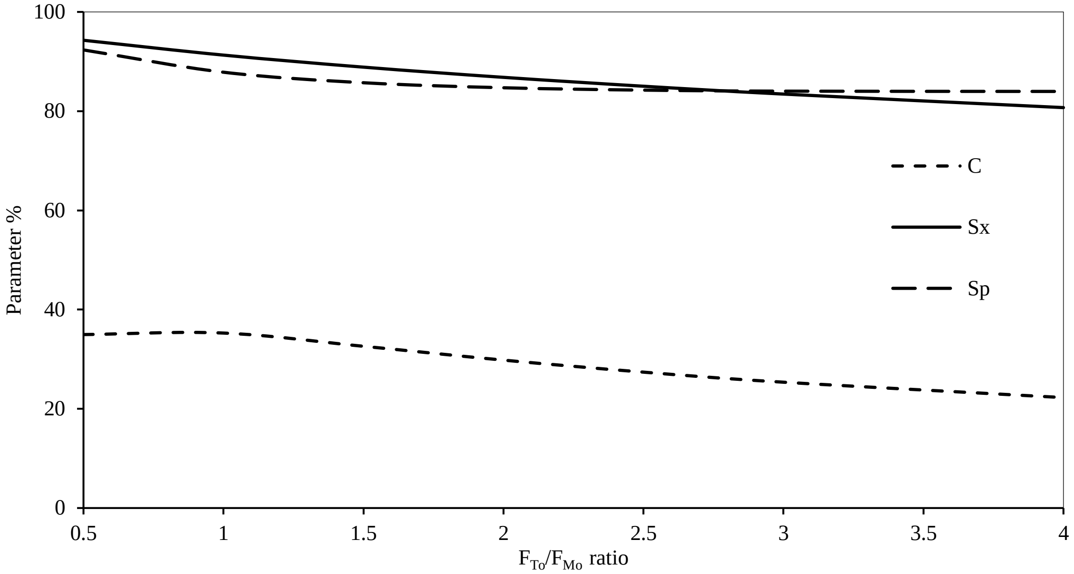


Figure 12. Effect of toluene-to-methanol feed ratio on conversion, selectivity of total xylenes, and selectivity of p-xylenes (temperature = 500 °C, Wcat/FTo = 15 g h/mol, pressure = 1 bar).

3.2.3. Effect of Pressure

Effect of pressure on toluene conversion, xylene selectivity and p-xylene selectivity is shown in Figure 13. The analysis is made at temperature of 500 °C with toluene-to-methanol feed ratio, F_{To}/F_{Mo}, of 1 and at space time, W_{cat}/F_{To}, of 15 g h/mol.

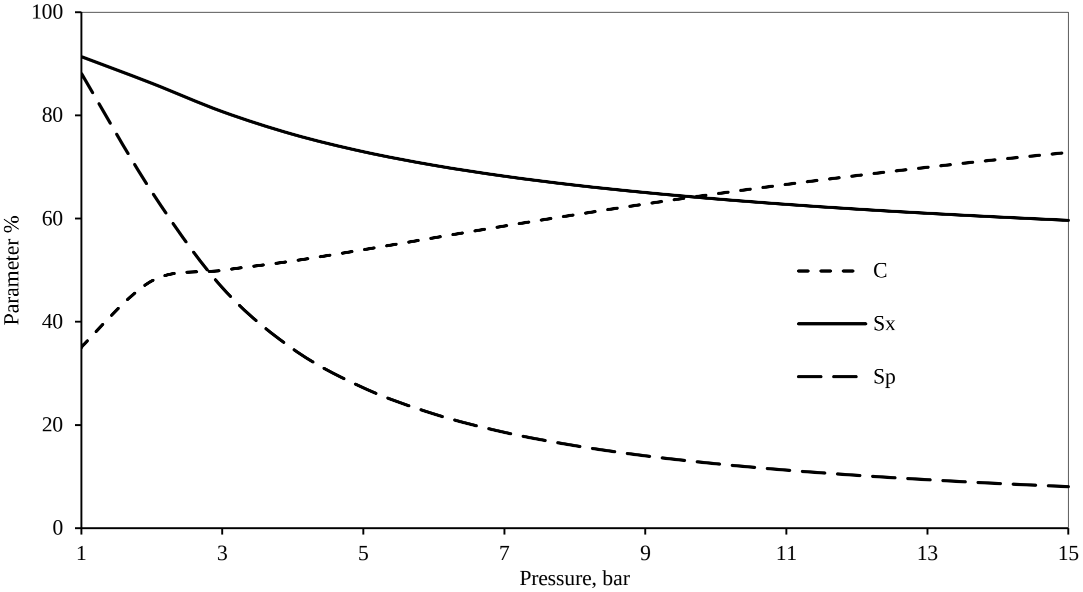


Figure 13. Effect of pressure on conversion, selectivity of total xylenes, and selectivity of p-xylenes (temperature = 500 °C, F_{To}/F_{Mo} = 1, W_{cat}/F_{To} = 15 g h/mol).

There is continuous increase in conversion C with increase in pressure. But there is decrease in total xylene selectivity and more significant decrease in selectivity of p-xylene S_p. This means increase in pressure increases toluene conversion towards side reactions. So, low pressure is favorable for high p-xylene selectivity.

3.2.4. Effect of the Space Time, W_{cat}/F_{To}

W_{cat}/F_{To} is the weight of catalyst per unit molar flow rate of toluene in the reactor feed. This is an important variable as by varying the catalyst weight to toluene flow ratio the space time or the contact time of reactant with the catalyst changes. As we have discussed it in section 2 the contact time effects the reaction occurring on the surface of catalyst. One important such reaction is the isomerization reaction which decreases the p-xylene selectivity. Figure 14 shows results of Aspen Plus® sensitivity analysis.

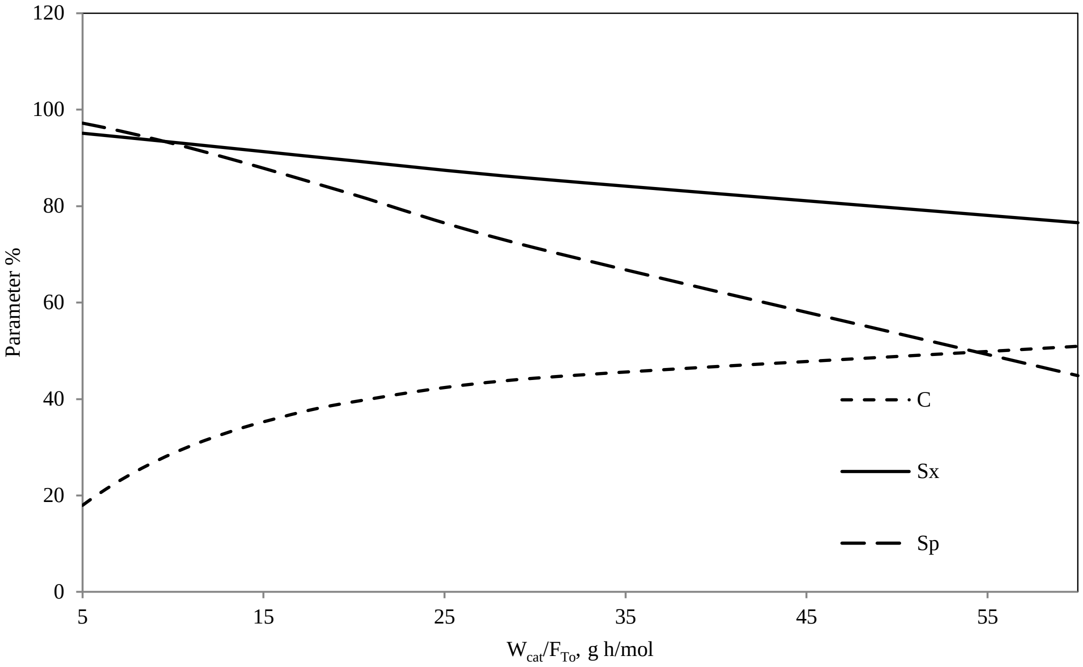


Figure 14. Effect of space time on conversion, selectivity of total xylenes, and selectivity of p-xylenes (F_{To}/F_{Mo} = 1, temperature = 500 °C, pressure = 1 bar).

This analysis shows that there is increase in conversion *C* with increase in space time, W_{cat}/F_{To}. p-Xylene selectivity S_P decreases sharply with increase in space time as the contact time increases. As reported by Breen et al. [9], low contact time increase the p-xylene selectivity by suppressing the unwanted isomerization of p-xylene at external catalyst surface. Low values of space time are favored for high p-xylene selectivity.

3.2.5. Effect of Water in the Reactor Feed

One of the undesired reactions in the toluene methylation process is the dehydration of methanol to water and gaseous hydrocarbons as shown in equation 2.2. This results in wastage of important raw material and generation of undesired compounds. Also this increases the separation difficulty due to production of large amount of water and gaseous hydrocarbons. One way to suppress this reaction is to introduce some amount of water in the reactor feed. Below are the results of sensitivity analysis showing effect of different amount of water on the reactor quality.

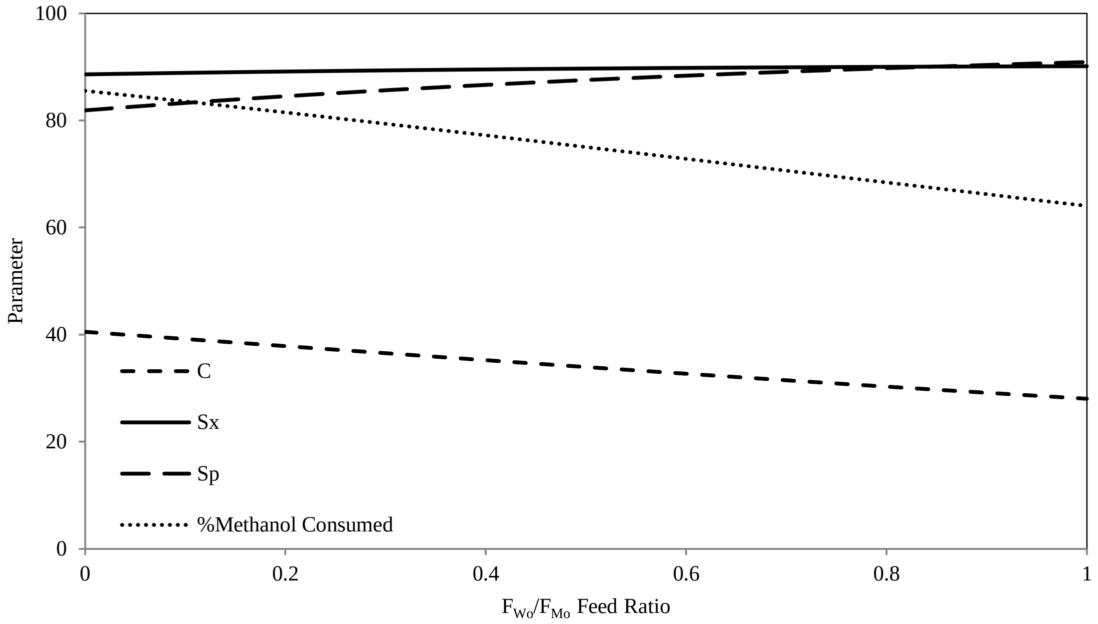


Figure 15. Effect of water in reactor feed (Temperature 500 °C, F_{To}/F_{Mo} ratio 1, W_{cat}/F_{To} 15 g h/mol, Pressure 1 bar).

As shown in Figure 15 with increase in amount of water fed the methanol consumption decreases. The xylene selectivity S_X and p-xylene selectivity S_P increase. However the effect on conversion C is inverse. Also the effect on methanol consumption is not very steep and we need to add large amount of water to get noticeable effects. This will result in large amount of water recycle and increase the separation difficulty and operating cost.

3.3. Optimization of Reactor Parameters

From sensitivity analysis made in section 3.2 it is found out that low temperature, low pressure, and low space time favors high p-xylene selectivity. The objective of this study is to develop a p-xylene production process from toluene methylation. To overcome the high separation cost of p-xylene from its close boiling isomers the p-xylene selectivity should be very high. This will reduce the separation cost and will also reduce the production of unwanted isomers, m-xylene and o-xylene.

In this section the process parameters of the reactor modeled in section 3.1 are optimized to get high p-xylene selectivity. Aspen Plus® Optimization tool [40] is used for this purpose. Sequential quadratic programming (SQP) algorithm is selected to solve the optimization problem

Although low pressure is advantageous, a pressure of 3 bars is selected. Pressure near atmospheric is not suitable from operation point of view because of pressure drop consideration across the packed bed reactor and the downstream separation processes. But a higher pressure than 3 bar lowers the p-xylene selectivity as shown in Figure 13. The rest of the process variables; temperature, space time W_{cat}/F_{To}, and toluene-to-methanol feed ratio F_{To}/F_{Mo}, are used as design variables. The objective, shown in equation 3.4, is maximum p-xylene selectivity and is defined in optimization tool input form using Fortran statement. Toluene feed flow rate is set to 1000 kmol/hr while values of catalyst loading, W_{cat}, and methanol feed flow rate, F_{Mo}, are used as adjustable variables for optimizing values of space time, W_{cat}/F_{To}, and methanol-to-toluene feed ratio, F_{To}/F_{Mo}. Methanol loss to side reactions of 40% is used as objective constraint; it is calculated as shown in equation 3.5 and inputted in optimization tool as a Fortran statement.

Objective: Maximize
$$S_p = \left(\frac{F_{p-X}}{F_{p-X}+F_{m-X}+F_{o-X}}\right) \times 100 \qquad (3.4)$$

Objective Constraint:

$$\%Methanol\ Loss = \frac{methanol\ reacted\ to\ form\ other\ than\ p-xylene}{total\ methanol\ reacted} \times 100 \quad \leq 40 \qquad (3.5)$$

Table 7 shows the initial values and the results of Aspen Plus® optimization tool and Table 8 shows the reactor simulation results using optimized process variables. p-Xylene selectivity is increased from 58.0% to 97.7% by optimizing the reactor temperature, toluene-to-methanol feed ratio, and space time; the optimum values are found to be 400 ºC, 2, and 2.5 g h/mol, respectively. Methanol loss to side reaction is also decreased from 82.4% to 40%. The optimized values of temperature and space time are lower than the initial values, which show that optimization results are in agreement with findings from the sensitivity analysis of section 3.2. Based on these results, a process is developed to separate p-xylene from the reaction products.

Table 7. Reactor Optimization Using Aspen Plus® Optimization Tool (Pressure = 3 bar)

	Temp ^{o}C	Space Time W_{cat}/F_{To}, g h/mol	F_{To}/F_{Mo}	Methanol loss to side reactions	C	S_x	S_p
Initial	500	15	1	82.4	35.0	86.6	58.0
Optimized	400	2.5	2	40.0	23.0	98.3	97.7

Table 8.Reactor simulation at optimized process variables

Name	Units	TOULENE	METHANOL	PRODUCT
Temperature	°C	400	400	400
Pressure	bar	3	3	3
Mole Flow	kmol/hr	1000	500	1588.64
Component Mole Flow				
Toluene	kmol/hr	1000	0	771.50
Methanol	kmol/hr	0	500	148.58
p-X	kmol/hr	0	0	218.64
Water	kmol/hr	0	0	374.84
Benzene	kmol/hr	0	0	2.70
GH	kmol/hr	0	0	67.18
m-X	kmol/hr	0	0	2.60
o-X	kmol/hr	0	0	2.60

Chapter 4: Development of Process Flow Diagram (PFD)

Based on the optimization results of section 3.3, Table 7, we can now make process flow diagram of the proposed process for the production of p-xylene from toluene methylation. The strategy for making the base case is to model the optimized reactor to get high p-xylene selectivity. Then based on the reactor outlet stream composition the separation processes is selected. Aspen Plus® is used for simulation with Peng-Robinsons property method. RadFrac block [40] is used for modeling distillation columns. Detail summary reports of the simulated equipment (blocks); pumps, distillation columns and heaters; are given in the Appendix.

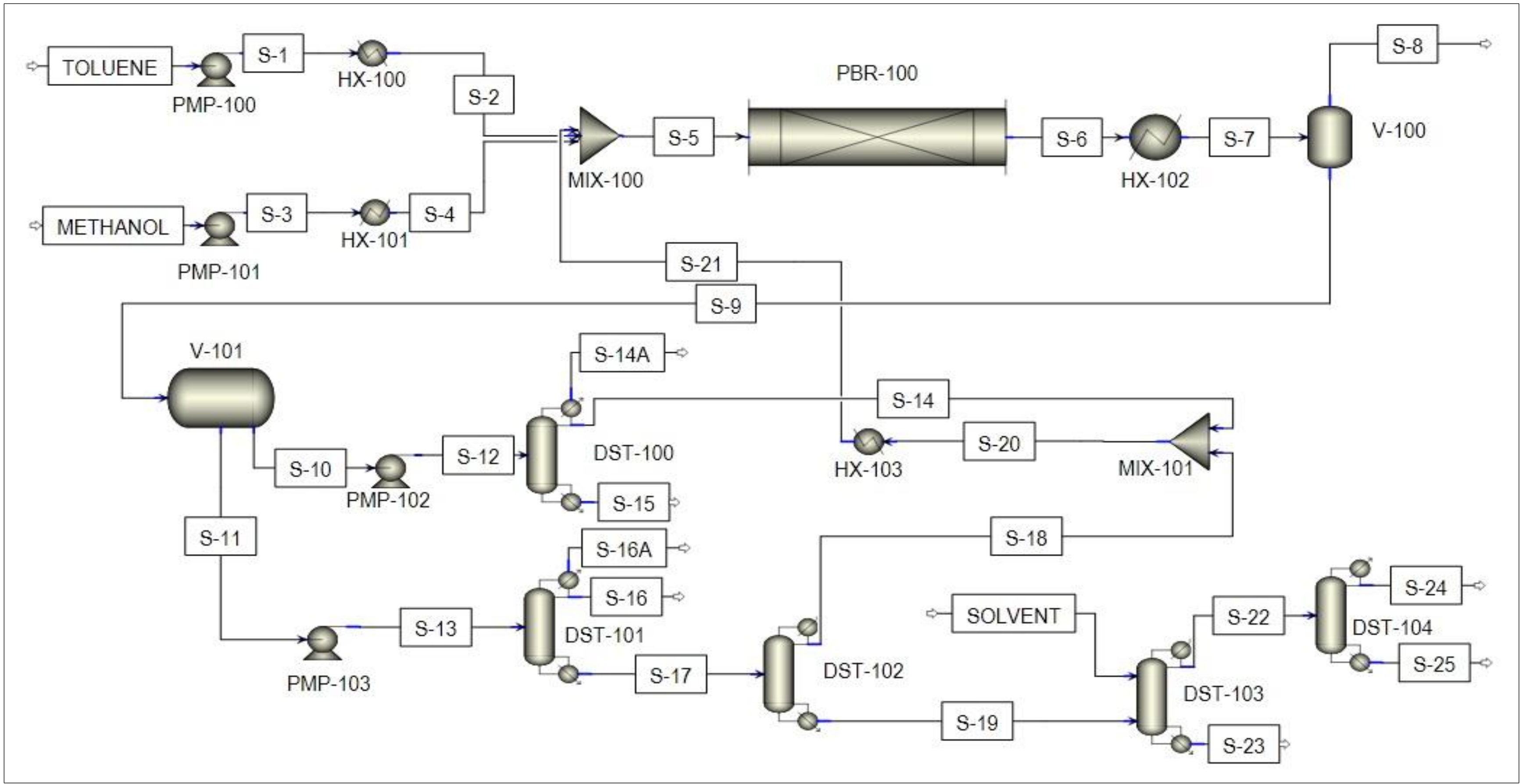
4.1. Development of PFD

Based on the reactor product stream the following PFD has been developed. The PFD is shown in Figure 16 and the corresponding stream data is shown in Table 9, followed by the description and detail of each process block.

Toluene and methanol are fed at temperature of 25 ^{o}C and pressure of 1 bar. The reaction will occur in gas phase at a temperature of 400 ^{o}C and pressure of 3 bars. Before entering the reactor we need to increase both temperature and pressure from atmospheric conditions to reactor conditions.

Feed Pumps PMP-100 and PMP-101: These are centrifugal pumps increasing the pressure of feed materials to 3 bars. PMP-100 pumps the feed toluene and PMP-101 pumps the feed methanol. The fresh feeds of toluene and methanol are set using Aspen Plus® design spec tool so that the reactor feed (stream S-5) is 1000 kmol/hr toluene and 500 kmol/hr methanol, respectively.

Feed Pre-Heaters HX-100 and HX-101: These are feed pre-heaters that increase the temperature of the feed raw materials to 400 ^{o}C. The phase of both feed materials changes from liquid to vapor. The heat load of HX-100 and HX-101 is 5733.5 kW and 6756.3 kW, respectively. Simple heater blocks are used in the simulation for calculation of heat loads.



Equipment Name	Description	Equipment Name	Description	Equipment Name	Description
PMP-100,101,102,103	Fluid Pumps	HX-100,101,102,103	Heat Exchanger	PBR-100	Packed Bed Reactor
V-100	Flash Vessel	V-101	Decanter Vessel	DST-100,101,102,103,104	Distillation Columns

Figure 16. Process flow diagram of p-xylene production from toluene methylation employing reactive distillation for the separation of the xylenes.

Table 9. Stream Data Table for p-Xylene Production from Methylation of Toluene

Stream Name		**TOLUENE**	**METHANOL**	**S-1**	**S-2**	**S-3**	**S-4**	**S-5**	**S-6**	**S-7**	**S-8**	**S-9**	**S-10**	**S-11**	**S-12**	**S-13**
Mole Flow	kmol/hr	215.24	393.65	215.24	215.24	393.65	393.65	1538.89	1609.77	1609.77	96.13	1513.65	437.16	1076.48	437.16	1078.28
Mass Flow	kg/hr	19831.89	12613.52	19831.89	19831.89	12613.52	12613.52	110549.50	110549.50	110549.50	2931.66	107617.90	9638.41	97979.47	9638.41	97751.62
Vapor Fraction		0.00	0.00	0.00	1.00	0.00	1.00	1.00	1.00	0.03	1.00	0.00	0.00	0.00	0.00	0.00
Temperature	^{o}C	25.00	25.00	25.06	400.00	25.03	400.00	399.95	400.00	50.00	51.42	51.42	40.00	40.00	49.46	44.38
Pressure	bar	1.01	1.01	3.00	3.00	3.00	3.00	3.00	2.99	2.49	1.20	1.20	1.20	1.20	10.50	8.50
Component Mole Flow																
Toluene	kmol/hr	215.24	0.00	215.24	215.24	0.00	0.00	1000.00	804.05	804.05	5.70	798.36	1.49	796.87	1.49	796.47
Methanol	kmol/hr	0.00	393.65	0.00	0.00	393.65	393.65	500.00	172.29	172.29	6.21	166.08	114.55	51.53	114.55	54.18
p-X	kmol/hr	0.00	0.00	0.00	0.00	0.00	0.00	18.31	204.52	204.52	0.56	203.96	0.13	203.83	0.13	200.91
Water	kmol/hr	0.00	0.00	0.00	0.00	0.00	0.00	16.86	344.57	344.57	20.42	324.15	317.82	6.33	317.82	7.67
Benzene	kmol/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.33	5.33	5.33	0.11	5.22	0.01	5.21	0.01	5.02
GH	kmol/hr	0.00	0.00	0.00	0.00	0.00	0.00	3.14	74.02	74.02	63.12	10.90	3.14	7.76	3.14	9.24
m-X	kmol/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.20	2.57	2.57	0.01	2.56	0.00	2.55	0.00	2.45
o-X	kmol/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.05	2.42	2.42	0.01	2.42	0.02	2.40	0.02	2.34
TBB	kmol/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DTBB	kmol/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TBMX	kmol/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Stream Name		**S-14**	**S-14A**	**S-15**	**S-16**	**S-16A**	**S-17**	**S-18**	**S-19**	**S-20**	**S-21**	**S-22**	**SOLVENT**	**S-23**	**S-24**	**S-25**
Mole Flow	kmol/hr	123.91	4.09	306.82	75.23	8.77	994.28	802.00	192.28	925.91	925.91	184.00	3.00	11.28	5.00	179.00
Mass Flow	kg/hr	3889.47	120.29	5551.94	2993.19	260.28	94498.15	74085.37	20412.77	77974.84	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	0.06	1.00	0.00	0.00	0.00	0.00	0.00
Temperature	^{o}C	70.87	70.87	145.09	74.25	74.25	212.83	156.21	187.37	136.15	400.00	136.99	150.00	156.56	78.13	113.94
Pressure	bar	4.00	4.00	4.20	8.00	8.00	8.20	3.00	3.20	3.00	3.00	1.00	1.50	1.10	0.40	0.50
Component Mole Flow																
Toluene	kmol/hr	1.53	0.02	0.00	7.87	0.08	788.51	788.41	0.10	789.95	789.95	0.10	0.00	0.00	0.04	0.06
Methanol	kmol/hr	108.39	1.23	1.75	52.90	1.29	0.00	0.00	0.00	108.39	108.39	0.00	0.00	0.00	0.00	0.00
p-X	kmol/hr	0.13	0.00	0.00	0.00	0.00	200.91	13.36	187.55	13.49	13.49	181.98	0.00	5.57	3.40	178.59
Water	kmol/hr	12.91	0.06	305.07	7.55	0.12	0.00	0.00	0.00	12.91	12.91	0.00	0.00	0.00	0.00	0.00
Benzene	kmol/hr	0.01	0.00	0.00	4.85	0.10	0.07	0.07	0.00	0.08	0.08	1.57	0.00	0.00	1.56	0.01
GH	kmol/hr	0.91	2.79	0.00	2.06	7.18	0.00	0.00	0.00	0.91	0.91	0.00	0.00	0.00	0.00	0.00
m-X	kmol/hr	0.00	0.00	0.00	0.00	0.00	2.45	0.14	2.32	0.14	0.14	0.00	0.00	0.00	0.00	0.00
o-X	kmol/hr	0.02	0.00	0.00	0.00	0.00	2.34	0.02	2.32	0.04	0.04	0.34	0.00	1.97	0.00	0.34
TBB	kmol/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.16	0.00	0.00
DTBB	kmol/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.00	1.26	0.00	0.00
TBMX	kmol/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.31	0.00	0.00

Packed Bed Reactor PBR-100: Packed bed reactor PBR-100 is the main block of the process flow sheet. It operates at the same conditions mentioned in section 3.3. Feed to the reactor is a mixture of fresh raw materials and toluene and methanol recycle stream S-21. The combined feed stream to the reactor is S-5 and the product stream is S-6. Weight of Mg ZSM-5 catalyst used is 2500 kg, giving W_{cat}/F_{To} ratio of 2.5 based on 1000 kmol/hr of toluene in S-5. A catalyst bed void fraction of 0.35 has been used.

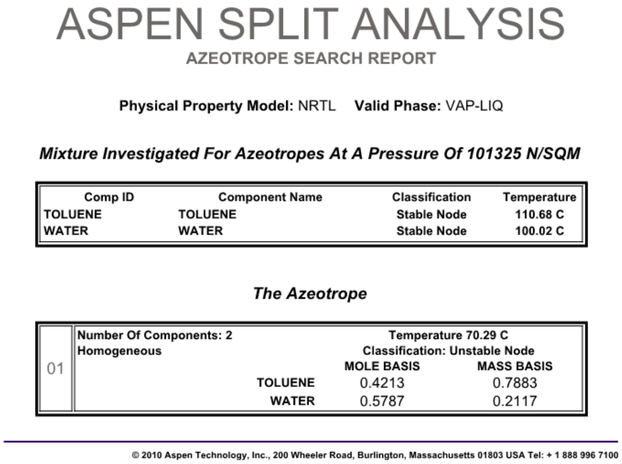
The reactor residence time is 0.267 sec. The total heat generated due to the exothermic reaction is -4116.8 W. This heat needs to be removed to keep the temperature at 400 ^oC. For this purpose a shell and tube type reactor is suggested in which catalyst is inside the tubes and on the shell side cooling media flows. This huge amount of energy generated can be used for the energy requirement of the process by steam generation.

Cooler HX-102: Heat exchanger HX-102 cools down the reactor product stream S-6. The product stream S-6 is in the vapor phase and contains unreacted toluene and methanol along with product xylenes and reaction by-products like water, benzene, and gaseous hydrocarbons. For separation purposes we need to condense the heavy components, then the light components like ethylene can be separated easily.

Temperature is decreased to 50 ^oC. This temperature is chosen on the basis of adequate ethylene separation and the fact that this cooling can be achieved with cooling water giving adequate temperature difference. The heat that needs to be removed is -34495.3 kW. Simple heater block is used to calculate the heat load.

Flash Vessel V-100: Flash vessel V-100 flashes the cooled two phase stream S-7 at a pressure of 2 bars to separate most of ethylene in the overhead stream S-8. 85% of ethylene fed is separated in the overhead stream S-8. The liquid stream, S-9, from V-100 goes to decanter V-101.

Decanter V-101: It is a decanter vessel separating the two liquid phases of S-9. Stream S-9 contains a mixture of water and immiscible nonpolar organic compounds like toluene and xylenes, while methanol is soluble in both water and organic phase. It is advantageous to separate these two phases before going to the distillation stage because toluene and water form an azeotrope. Figure 17 shows the results of Aspen Plus Split Analysis® report.



ASPEN SPLIT ANALYSIS

AZEOTROPE SEARCH REPORT

Physical Property Model: NRTL **Valid Phase:** VAP-LIQ

Mixture Investigated For Azeotropes At A Pressure Of 101325 N/SQM

Comp ID	Component Name	Classification	Temperature
TOLUENE	TOLUENE	Stable Node	110.68 C
WATER	WATER	Stable Node	100.02 C

The Azeotrope

01	Number Of Components: 2		Temperature 70.29 C	
	Homogeneous		Classification: Unstable Node	
			MOLE BASIS	MASS BASIS
		TOLUENE	0.4213	0.7883
		WATER	0.5787	0.2117

Figure 17. Aspen split analysis report.

The organic phase containing toluene, benzene and xylenes can be separated from water by gravity settling in a decanter. The results of decanter V-101 are water rich stream S-10 and organic rich stream S-11. Now we move to distillation for further separation.

Methanol Column DST-100: The water rich stream from decanter V-100 contains a large amount of methanol. This methanol needs to be separated and recycled back to the reactor. Distillation column DST-100 is used for this purpose. Aspen Plus RadFrac block is used for modeling DST-100. Methanol being the light key leaves at the top as distillate stream S-14. S-14 is sent to recycle heater HX-103. Water is obtained in the bottom stream S-15, and sent out of the process for further treatment or wasted.

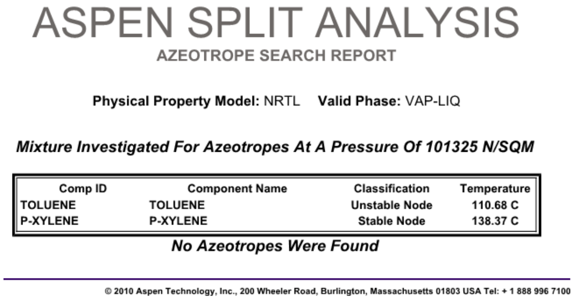
The column is operated at 4 bar pressure to get suitable temperature in the condenser, 70.8℃. The details of the column summary are given in Table A.2 in the Appendix.

Purge Column DST-101: The organic rich stream, S-11, form decanter V-101 mostly contains toluene and xylenes. Before we can separate toluene and xylenes we need to separate benzene and other light components, so that our recycle stream becomes rich in toluene. This will also create purge for these light components so that there is no accumulation of these components in the continuous process.

Aspen Plus® RadFrac block is used for modeling. The operating pressure for the column is 8 bars. The bottom stream S-17 contains the heavy key toluene and xylenes and the distillate stream S-16 contains light components that are vented for purge. Detail summary of the column is given in Table A.2 in the Appendix.

Toluene Column DST-102: The bottom stream S-17 of DST-101 contains toluene and xylenes. The boiling points of toluene and p-xylene are 110.6℃ and 138.3℃, respectively. Aspen Split Analysis report in Figure 18 shows that there is no formation of azeotrope and they can be separated by distillation. DST-102 separates toluene from xylenes. The toluene being the lighter key is obtained as distillate. The distillate stream S-18 is mixed with recycled methanol in MIX-101 and recycled back to the reactor through recycle heater HX-103. The bottom stream S-19 from DST-102 contains 97.5% of p-xylene and the rest is o-xylene, m-xylene and toluene.

The column is operated at 3 bar pressure, the results of Radfrac column are given in Table A.2 in the Appendix.



ASPEN SPLIT ANALYSIS

AZEOTROPE SEARCH REPORT

Physical Property Model: NRTL **Valid Phase:** VAP-LIQ

Mixture Investigated For Azeotropes At A Pressure Of 101325 N/SQM

Comp ID	Component Name	Classification	Temperature
TOLUENE	TOLUENE	Unstable Node	110.68 C
P-XYLENE	P-XYLENE	Stable Node	138.37 C

No Azeotropes Were Found

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Figure 18. Toluene and p-xylene split analysis report

Recycle Heater HX-103: This is a recycle stream heater. The two streams S-14 and S-18 are methanol and toluene recycle streams, respectively. These are mixed and passed through this heat exchanger to increase the temperature of mixed stream S-20 to 400 ^{o}C. The heated stream S-21 is at 400 ^{o}C temperature and 3 bar pressure. The heat load of the heater is 18872.6 kW. It contains 788.4 kmol/hr toluene and 108.3 kmol/hr methanol. The makeup toluene and methanol are added from fresh raw materials to make the total flow 1000 kmol/hr and 500 kmol/hr, respectively.

4.2. p-Xylene Separation

Industrial purity requirement for p-xylene is 99.5% while 99.8% is ultrapure pure p-xylene [1]. The bottom stream from DST-102 is a mixed xylene stream with 97.5% p-xylene. It is a challenge to separate p-xylene from its isomers due to the very close boing points as shown in Table 3. The technologies mostly used these days for xylene separation are adsorption and crystallization [1]. But here these techniques pose a serious problem as the p-xylene stream is already 97.5% pure. In adsorption, the simulated moving bed (SMB) technology is used [17]; but p-xylene is the one that is being adsorbed due to its smaller kinetic diameter (kinetic diameter: 6.7 Å for p-xylene, 7.3 Å for o-xylene, and 7.4 Å for m-xylene [19]). This means a large adsorption bed would be required for separation which is not economical. The same dilemma exists with crystallization as crystallizing out the 97.5% of a stream is not feasible.

The other option for xylene separation is by distillation, as discussed in section 1.3.3. o-Xylene can be separated from p-xylene by extensive distillation as the relative volatility is around 1.17. m-Xylene and p-xylene, can be hardly separated by ordinary distillation due to a relative volatility of around 1.02. Saito el al. [20] reported the separation of m-xylene from p-xylene by reactive distillation. m-Xylene reacts preferentially with di-tertiary butyl-benzene (DTBB) and tertiary butyl-benzene (TBB) to form tertiary butyl m-xylene (TBMX) and benzene (B). For modelling the reactive distillation column in Aspen Plus® the reaction can be assumed to reach equilibrium [21].

Reactive Distillation Column DST-103: Stream S-19 is fed to reactive distillation column DST-103. The column operates at 1 bar pressure which results in suitable temperature in the condenser, 137 ºC, for cooling water to be used as coolant. The equilibrium reactions shown in equations 1.1 and 1.2 are added to distillation block along with equilibrium constants given in equations 1.3 and 1.4. Solvent stream containing DTBB and TBB is added at 10th stage (from top) of distillation column. Separation of o-xylene requires large number of trays, high reflux ratio, and high reboiler duty.

To get optimum results a sensitivity analysis is made. Mole fraction of p-xylene in the distillate and mole fraction of o-xylene in the bottom are set using design spec tool within the RadFrac environment, to 0.99 and 0.16, respectively. These values of composition results in 99.7% p-xylene purity in the product stream S-25. Reflux ratio and distillate rate are varied to get the set values of compositions in the column top and bottom. Now for each set of total equilibrium stages (including condenser and reboiler) and feed stage location the RadFrac block converges only if the design spec tool also converges.

Then NQ Curves tool, available in RadFrac block [40], is used to find the optimum location of the feed stage that gives minimum reboiler duty. The results of this analysis are shown in Table 10 for total equilibrium stages of 40 to 60. As shown in the table there is tradeoff between total equilibrium stages and reboiler duty. Higher than 50 equilibrium stages does not result in significant decrease in reboiler duty, so 50 equilibrium stages are used with feed stage location of 21 in DST-103.

Table 10. Results of NQ Curves Analysis for Reactive Distillation Column DST-103.

Number of Stages	Feed Stage Location	Molar Reflux Ratio	Distillate Rate	Reboiler Duty	p-Xylene Product Purity
			kmol/hr	kW	
40	21	22.95	183.78	43931.9	99.7
45	20	11.19	183.74	22042.7	99.7
50	21	7.99	183.72	16097.3	99.7
55	21	7.18	183.70	14586.8	99.7
60	21	6.63	183.70	13572.5	99.7

DST-103 Profiles: Figure 19 shows the composition profiles of o-xylene and m-xylene in DST-103. The stage number increases from the top of distillation column. The composition of m-xylene decreases due to reaction with DTBB and TBB while composition of o-xylene decreases due to high reflux ratio and high reboiler duty; 9286.2 kW and 16096.8 kW, respectively. Figure 20 shows the temperature and p-xylene composition profile in DST-103.

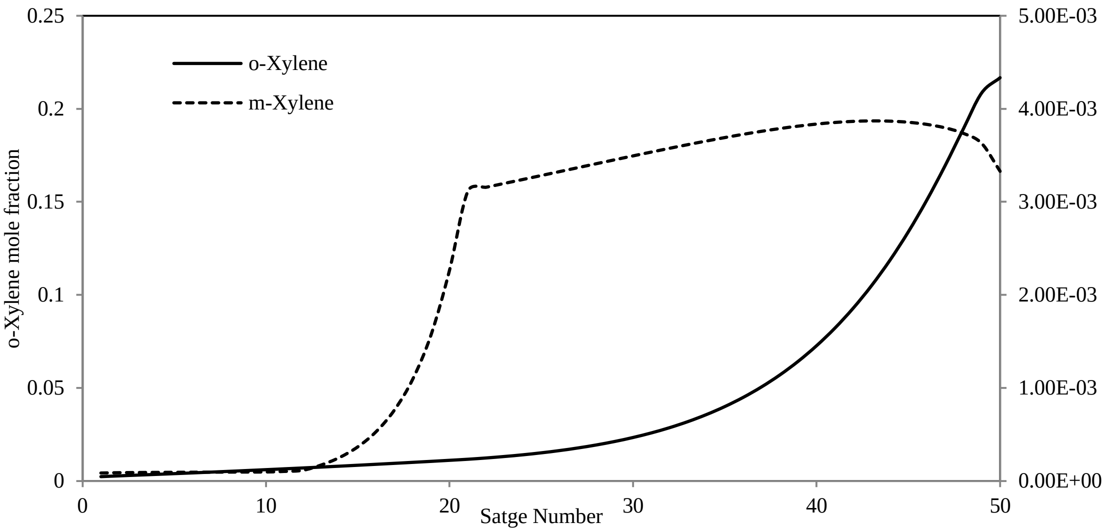


Figure 19. Composition profile of m-xylene and o-xylene in reactive distillation column DST-103.

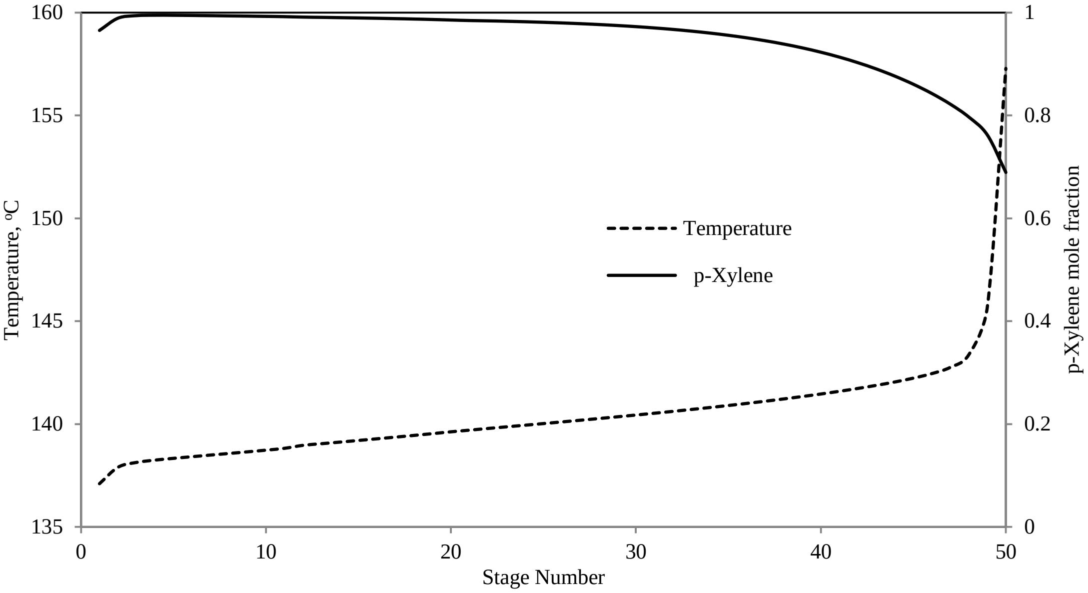


Figure 20. p-Xylene composition and temperature profile for reactive distillation column DST-103.

DST-104: Distillate stream S-22 contains almost no m-xylene and most of o-xylene is also separated, but it contains the produced benzene which lowers the purity. S-22 is sent to distillation column DST-104 where the light component benzene is separated. The column operates at 0.4 bar pressure with condenser temperature of 78.2℃. The product stream S-25 comes from the bottom of DST-104 and meets the purity specification of 99.7%. More details of the column are given in Table A.2 in the Appendix.

4.3 Waste Streams

Compounds involved in this process, like benzene, are carcinogenic. Proper management of the waste streams is important for safe operation of the process and environment. Environmental impact of the process is not in the scope of present study; however analysis of major waste streams is discussed below.

Stream S-15 is the waste water stream, water is produced as side product in toluene methylation reaction. This stream needs to be treated before wasting so that COD (chemical oxygen demand) is at the allowable limit. Stream S-8, S-14A, S-16A, S-23 and S-24 contain GH (gaseous hydrocarbons) and aromatics, they can be purified and sold but it will require a separate treatment section and will add more cost to process. Other option is to burn them as fuel in the furnace. A vent pipe can be designed in which all these waste stream can be fed. The vent pipe can safely transport these materials to either treatment process or to furnace for burning.

Chapter 5: Second Law Analysis for the Process

The process developed in section 4 produces 99.7% pure p-xylene from toluene methylation by using reactive distillation for p-xylene separation. The process flow diagram developed is shown in Figure 16. To make the process more competitive and highlight the areas of improvement a second law analysis is made. The lost work is calculated around each block of the process flow diagram and then a comparison is made between different blocks. This highlights the areas which are less thermodynamically efficient and increases the understanding about each process block.

5.1 Second Law Analysis and Basis

The objective of this study is to determine the lost work for each block based on second law analysis. Lost work, $L\dot{W}$, also known as loss of availability or loss of exergy is the entropy generated, $\Delta\dot{S}$, multiplied by surrounding temperature, t_o, as shown in equation (5.1) [41]. Lost work is calculated around each block of the process flow diagram, Figure 16, by using equation (5.2) [41].

$$L\dot{W} = t_o \times \Delta\dot{S} \tag{5.1}$$

$$L\dot{W} = \left[\Sigma\dot{A}_{in} - \Sigma\dot{A}_{out}\right] + \left[\Sigma\dot{W}_{in} - \Sigma\dot{W}_{out}\right] + \left[\Sigma\left\{\dot{Q}(1-\tfrac{t_o}{t})\right\}_{in} - \Sigma\left\{\dot{Q}(1-\tfrac{t_o}{t})\right\}_{out}\right] \tag{5.2}$$

The first bracket in equation (5.2) represents the net rate of availability function around a block, second bracket is the net rate of work, and the third bracket is the net rate of heat multiplied by the Carnot cycle efficiency. $\dot{A}$ is availability function defined in equation (5.3) [41], $\dot{W}$ is rate of work, and $\dot{Q}$ is rate of the heat transfer. Availability function, $\dot{A}$, of each stream in the process flow diagram is calculated by enthalpy flow, $\dot{H}$, entropy flow, $\dot{S}$, and temperature data reported in the stream results of Aspen Plus® simulation. Work, $\dot{W}$, and heat, $\dot{Q}$, data around each block of the process flow diagram is taken from the equipment summary report in Aspen Plus®, given in the Appendix. These values are exported to MS Excel and lost work around each block is calculated by using equations (5.2) and (5.3).

$$\dot{A} = \dot{H} - t_o \times \dot{S} \tag{5.3}$$

Following conventions and assumptions are used in making the second law analysis: surrounding temperature, t_o, is assumed to be 25 °C (298.15 K), surrounding pressure is assumed to be 1.01325 bar, heat removed from block is assumed to be at temperature of cooling media [41], heat added to a block is assumed to be at the temperature of heating media [41], cooling water temperature is assumed to be 25 °C (298.15 K), this makes condensers contribution to lost work zero, as $t = t_o$, HP steam at 250 °C, is assumed for heating in the reboilers and heaters and zero heat loss to the surrounding.

5.2 Second Law Analysis Results and Discussion

Using equations (5.2) and (5.3) along with the assumptions mentioned in the previous section lost work is calculated around each block of the process flow diagram, Figure 16. The results are shown in Table 11. Each of the three brackets in equation (5.2) is calculated separately and then added to calculate the lost work, $L\dot{W}$. In the last column the percentage of lost work, $\%L\dot{W}$, is calculated.

All the pumps and the two vessels, V-100 and V-101, offer insignificant lost work generation. From the heater blocks, the HX-102 has highest lost work, 18.9%, due to large change in temperature and high mass flow rate. HX-102 is the cooler, after the reactor PBR-100, which cools the reactor product stream from reaction temperature of 400 °C to 50 °C. The second highest $L\dot{W}$ among the heater blocks is HX-103, 7.0%, which heats the toluene and methanol recycle streams to the reaction temperature. Reactor PBR-100 also has significant lost work generation due to the removal of the large heat of reaction, - 4116.8 kW. The distillation columns, except DST-100, have high lost work generation due to high reboiler duties. Reactive distillation DST-103 has the highest lost work, 21.9%, due to large the heat duty required for separation of o-xylene from p-xylene.

From the results it is found that the heater block DST-102 and the distillation blocks DST-101, DST-102 and DST-103 have the highest lost work generations. In distillation blocks the high lost work is due to the high reboiler duties required. These lost works due to heat can be reduced by proper heat integration of the process through pinch technology.

Table 11. Second Law (Lost Work) Analysis for Toluene Methylation Process

Name of Block	Change in Stream Availability	Work	Heat	Temp	Heat Equivalent of Work	Lost Work	% Lost Work
	$\Sigma\dot{A}_{in} - \Sigma\dot{A}_{out}$	$\Sigma\dot{W}_{in} - \Sigma\dot{W}_{out}$	$\dot{Q}$	t	$\Sigma\left\{\dot{Q}(1-\frac{t_o}{t})\right\}_{in} - \Sigma\left\{\dot{Q}(1-\frac{t_o}{t})\right\}_{out}$	$L\dot{W}$	$\%L\dot{W}$
	kW	kW	kW	ºC	kW	kW	
PMP-100	-1.5	1.5				0.1	0.0
PMP-101	-1.0	1.1				0.0	0.0
PMP-102	-1.2	1.3				0.1	0.0
PMP-103	53.5	29.0				82.5	0.2
MIX-100	439.0					439.0	0.9
MIX-101	268.1					268.1	0.6
V-100	62.7					62.7	0.1
V-101	3.1					3.1	0.0
HX-100	-1982.6		5733.5	400.00	3194.0	1211.4	2.6
HX-101	-1664.0		6756.3	400.00	3763.8	2099.8	4.5
HX-102	11472.2		-34495.3	50.00	-2668.7	8803.5	18.9
HX-103	-7248.4		18872.6	400.00	10513.6	3265.2	7.0
PBR-100	5300.4		-4116.8	250.00	-1770.6	3529.8	7.6
DST-100	-204.1		3613.3	250.00	1554.0	1349.9	2.9
DST-101	-2445.1		20294.4	250.00	8728.3	6283.3	13.5
DST-102	761.8		17592.5	250.00	7566.3	8328.1	17.9
DST-103	190.8		23260.0	250.00	10003.8	10194.7	21.9
DST-104	59.1		1163.0	250.00	500.2	559.3	1.2
					Total	**46480.60**	**100.00**

Chapter 6: Heat Integration

From the results of the second law analysis it is concluded that heat integration of the process should be investigated in order to reduce the lost work generation. Aspen Energy Analyzer® [42] is used for heat integrating the process. The objective of the study is to design a heat network that gives minimum total cost. The assumptions and conventions used are mentioned in the next sections. Aspen Energy Analyzer® solves the heat integration problem by solving the superstructures to minimize the total annual cost [42]. Some of the terms used in the Apsen Energy Analyzer® are defined below.

- ***Process Stream:*** a stream containing fluid which needs to be cooled or heated. As a minimum, Aspen Energy Analyzer® requires to specify the name of the process stream, inlet temperature, outlet temperature, and *MCp* or enthalpy change [42].
- ***MCp Parameter:*** *MCp* is the product of the specific heat capacity of the process stream, *Cp*, and the mass flow rate of the process stream [42]. Equation (6.1) is used to calculate *MCp*. The *MCp* of a stream is usually constant when the temperature difference is not great. However, for large change in temperature and/or phase change the *MCp* change can be significant and proper segmentation of the stream is required.

$$MCp = \frac{dH}{dt} \tag{6.1}$$

- ***Enthalpy Parameter:*** is the change in enthalpy of the stream when it is heated or cooled. It is used for calculating the *MCp* parameter by using equation (6.1) [42]. In Aspen Energy Analyzer® either *MCp* or enthalpy change data is required for specifying a stream. When the change in enthalpy with temperature is not linear segmentation of the stream is required [42], as in the case of phase change stream or high temperature change stream.
- ***Utility:*** a hot or cold stream that is not part of the process streams but is required to fulfill the heating and cooling requirement of the process streams.

6.1. Process Stream Input

The stream data is generated from Aspen Plus® simulation model developed in section 4.0 and exported to Aspen Energy Analyzer®. Table 12 shows all the process streams which need to be cooled or heated. Streams requiring temperature increase are classified as cold streams and the ones requiring temperature decrease are classified as hot streams. For inputting the reboilers and the condensers in the heat integration problem, the convention is to assume a hypothetical 1 °C change in temperature with enthalpy change equal to the latent heat required. Distillation column condensers and reboilers are named with block name followed by the abbreviation Cond for condenser and Reb for reboilers, i.e. DST-100 condenser is inputted as DST-100_Cond. Heat removed from the reactor PBR-100 is also included in the process streams by using a hypothetical 1 °C cooling and change in stream enthalpy equal to the heat of reaction in PBR-100.

Table 12. Process Stream Input Data for Heat Integration

Name	Classification	Inlet t	Outlet t	Enthalpy Change
		°C	°C	kW
S-1	Cold	25	400	5733.965
S-3	Cold	25	400	6756.639
S-20	Cold	136	400	18904.045
S-7	Hot	400	50	34882.554
PBR-100	Hot	400.5	399.5	4116.79
DST-100_Cond	Hot	71	70	2969.47
DST-100_Reb	Cold	144.5	145.5	3613.33
DST-101_Cond	Hot	75.5	74.5	11220.28
DST-101_Reb	Cold	212	213	20294.36
DST-102_Cond	Hot	157	156	20640.42
DST-102_Reb	Cold	187	188	17592.5
DST-103_Cond	Hot	137.5	136.5	23865.44
DST-103_Reb	Cold	156	157	23260
DST-104_Cond	Hot	79	78	1426.82
DST-104_Reb	Cold	113.5	114.5	1163

6.1.1. Stream Segmentation

For large change in temperature and/or phase change, proper segmentation of the stream is required so that enthalpy vs temperature data is linear and the *MCp* value calculated is accurate in each temperature subinterval. Figure 21 shows the enthalpy vs temperature graph of stream S-1. The enthalpy vs temperature data is generated by using the sensitivity analysis tool available in Aspen Plus® [40]. Stream S-1 is heated from 25 °C to 400 °C and there is phase change involved resulting in non-linear relation between enthalpy and temperature. This stream is manually segmented, as shown in Table 13, so that enthalpy vs temperature data is linear in each segment and results in relatively accurate calculation of *MCp*. The segmentation is also plotted in Figure 21 and it closely matches the actual curve.

Table 13. Segmentation Data of Process Stream S-1

Name	**t_{in}**	**t_{out}**	**Enthalpy Flow**
	°C	°C	kW
Segment 1	25	155	1299.521
Segment 2	155	156	1807.195
Segment 3	156	300	1451.022
Segment 4	300	400	1176.231

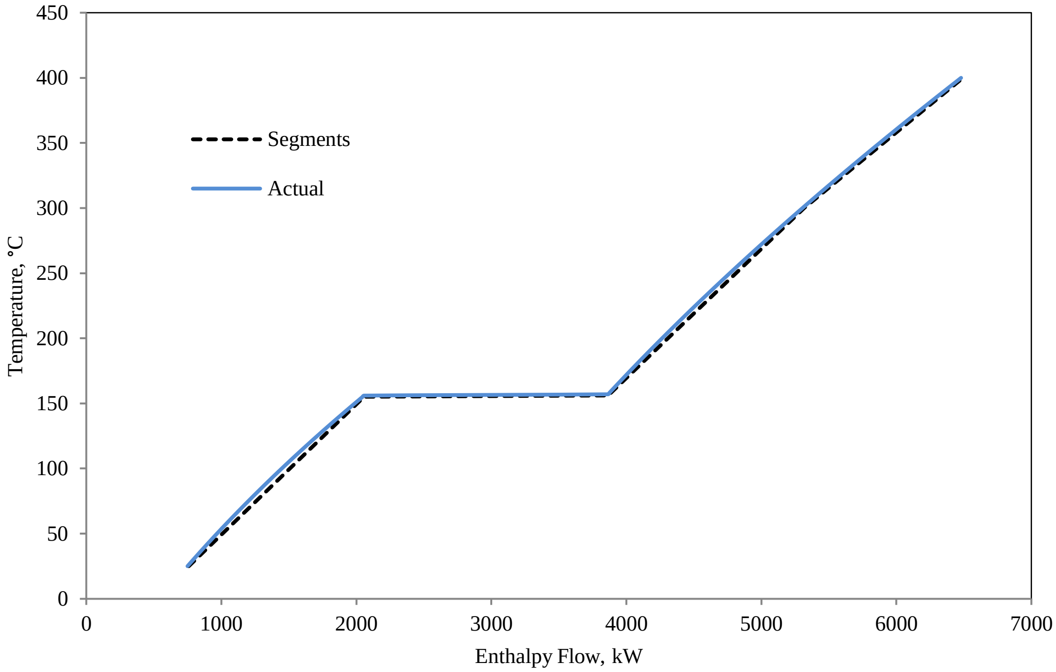


Figure 21. Enthalpy vs temperature for stream S-1.

A similar procedure is followed for streams S-3, S-7, and S-20 which have non-linear enthalpy vs temperature relation. The rest of the streams, undergoing a phase change, are assigned 1 °C hypothetical change and do not need segmentation.

6.1.2. Heat Transfer Coefficient (HTC)

Typical values of the heat transfer coefficient available in Aspen Energy Analyzer® are used for heat integrating the process. Values of HTC coefficient and the streams for which they are used are given in Table 14.

Table 14. Heat Transfer Coefficient Data [42]

Stream Type	HTC	Process Streams
	kJ/hr m^2 °C	
Aromatic Vapors	1415.1	Vapor Segments of Stream S-1, S-3, S-7 and S-20. DST-101_Cond, DST-102_Cond, DST-103_Cond,DST-104_Cond
Condensing/Reboiling Stream	21600	PBR-100, DST-100_Cond
Organic Liquids	2628.1	Liquid Segments of Stream S-1, S-3, S-7 and S-20. DST-100_Reb, DST-101_Reb,DST-102_Reb, DST-103_Reb, DST-104_Reb
Water	9198.4	Cooling Water Utility

6.2. Utilities

After analyzing the temperature levels of the process streams in Table 12, two hot utilities and two cold utilities are selected from Aspen Energy Analyzer® utilities data bank [42]. These utilities are as shown in Table 15 . To heat the process streams up to 400 °C Fired Heater utility is needed. While the rest of hot utilities are provided by HP steam at 250 °C which is sufficient to provide the heating in all the reboilers and also the preheating of streams S-1, S-3 and S-20. For removing heat in the isothermal reactor PBR-100 HP Steam Generation cold utility is used. HP Steam Generation cold utility has negative cost/energy as it can be used for making up HP steam hot utility requirement. The second cold utility is Cooling Water which is sufficient to provide cooling up to lowest temperature of the process streams.

Table 15. Utilities for Heat Integration of Toluene Methylation Process [42]

Name of Utility	Classification	t_{in}	t_{out}	Cost/Energy	HTC
		°C	°C	$/kJ	kJ/hr m^2 °C
Fired Heat (1000)	Hot	1000	400	4.25E-06	399.6
HP Steam	Hot	250	249	2.50E-06	21600
Cooling Water	Cold	25	40	2.12E-07	13500
HP Steam Generation	Cold	249	250	-2.49E-06	21600

6.3. Cost Basis for Heat Integration

Aspen Energy Analyzer® generates different layouts (designs) of the heat integration problem by solving superstructures. The objective of this study is to compare generated designs based on the relative total cost and not the absolute determination of cost [42]. Hence, default cost parameters available in Aspen Energy Analyzer® cost databank are used. All the heat exchangers are assumed to be shell and tube heat exchangers and equation (6.2) is used to find the capital cost of the exchanger [42]. Equation (6.3) is used to calculate the capital cost of furnaces [42].

$$CC_{he} = a + b\left(\frac{Area}{N_{shell}}\right)^{c} \times N_{shell} \tag{6.2}$$

$$CC_{f} = a + b(Duty)^{c} \tag{6.3}$$

where

CC_{he} = installed capital cost of heat exchanger

CC_f = installed capital cost of furnace

a = installation cost of a heat exchanger

b, c = duty and area related cost parameters

$Area$ = heat transfer area of a heat exchanger

N_{shell} = number of shells in heat exchanger

$Duty$ = amount of energy being transferred in a heat exchanger

The default values of factors a, b, and c available in Aspen Energy Analyzer® are used; 1000, 800, and 0.8, respectively [42].

Operating Cost (OC): it is calculated by using equation (6.4).

$$OC = \Sigma(C_{hu} \times Q_{hu}) + \Sigma(C_{cu} \times Q_{cu}) \tag{6.4}$$

where

OC = operating cost , \$/yr.

C_{hu}, C_{cu} = cost of hot and cold utilities per unit energy, \$/kJ, given in Table 15.

Q_{hu} = energy target of hot utility, kW.

Q_{cu} = energy target of cold utility, kW.

Total Annual Cost (TAC): accounts for both operating and capital cost of the heating network, it is calculated by equation (6.5) [42], where Λ is annualization factor calculated by equation (6.6).

$$TAC = \Lambda \times CC + OC \tag{6.5}$$

$$\Lambda = \frac{(1+\frac{ROR}{100})^{PL}}{PL} \tag{6.6}$$

The default values of 10% and 5 years are used for ROR (rate of return) and plant life (PL), respectively [42]. *TAC* is minimized in solving superstructures [42].

6.4. Optimum Minimum Approach Temperature (ΔT_{min})

After specifying the process and utility streams along with the cost basis, the optimum minimum approach temperature is selected. Range Target tool available in Aspen Energy Analyzer [42], is used to analyze the effect of different ΔT_{min} on the total annualized cost, *TAC*.

The results are shown in Figure 22, and ΔT_{min} of 12 °C gives the minimum TAC of 0.213 \$/sec or 6.743×10^{6} \$/yr. Figure 23 shows the composite curve at ΔT_{min} of 12 °C. Figure 24 shows the energy targets for maximum energy recovery (MER), the minimum cooling and heating load, the minimum area targets required along with the minimum cost targets and pinch temperatures.

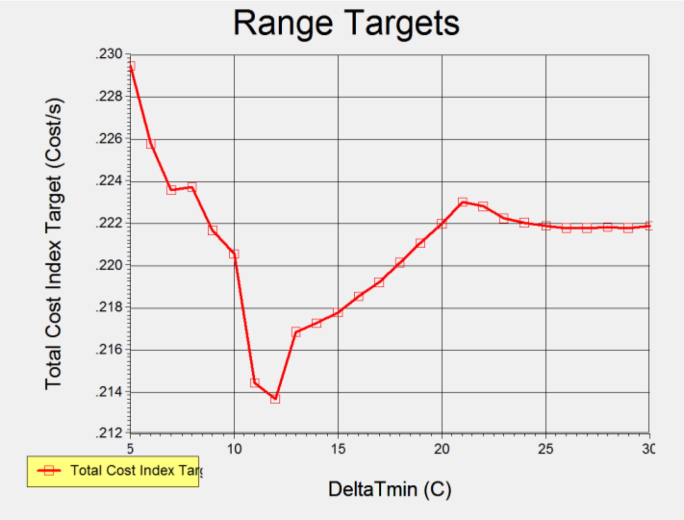


Figure 22. Range Targets tool analysis of the effects ΔT_{min} on TAC.

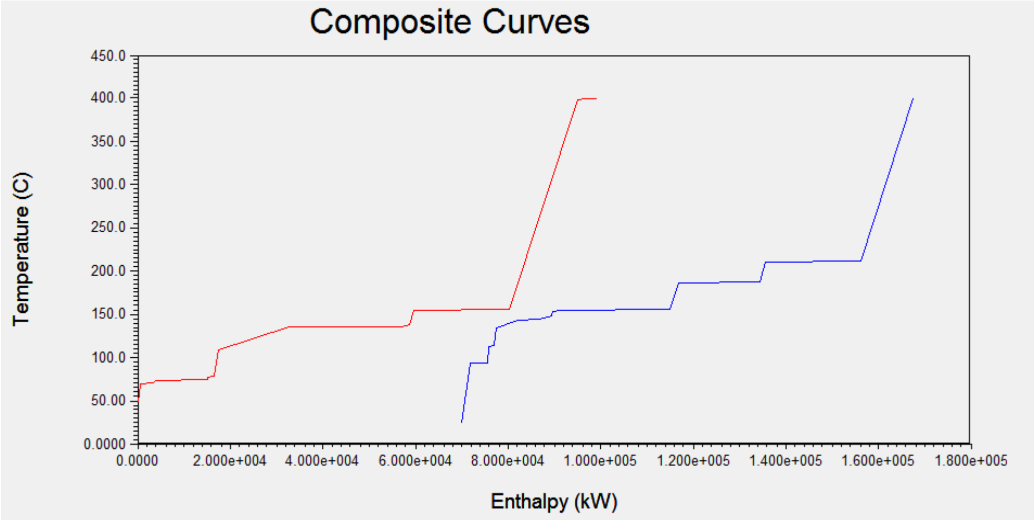
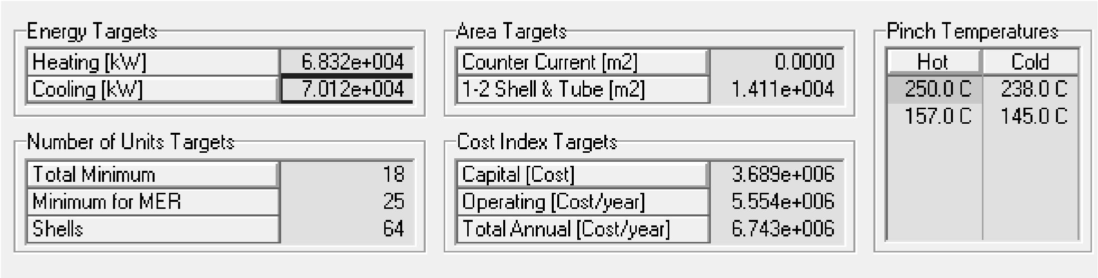


Figure 23. Composite curves for heat integration of toluene methylation process at ΔT_{min} of 12 °C.



Energy Targets

Heating [kW]	6.832e+004
Cooling [kW]	7.012e+004

Area Targets

Counter Current [m2]	0.0000
1-2 Shell & Tube [m2]	1.411e+004

Pinch Temperatures

Hot	Cold
250.0 C	238.0 C
157.0 C	145.0 C

Number of Units Targets

Total Minimum	18
Minimum for MER	25
Shells	64

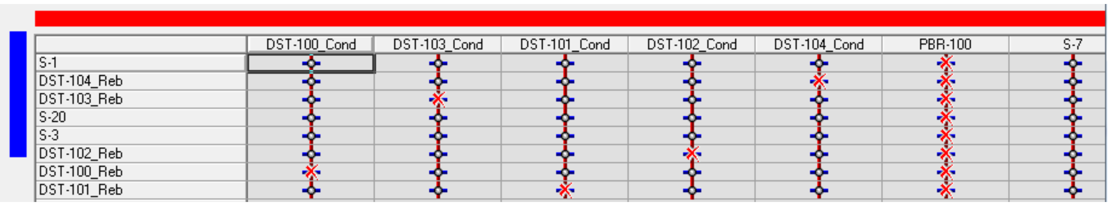
Cost Index Targets

Capital [Cost]	3.689e+006
Operating [Cost/year]	5.554e+006
Total Annual [Cost/year]	6.743e+006

Figure 24. Heat integration targets.

6.5. Heat Network Designs

Some of the streams which are impractical to match and can lead to operation problems are specified in the input as forbidden matches, as shown in the Figure 25. Red cross over heater icons show the forbidden or impractical matches. In PBR-100 heat can only be removed by cold utility as adding process stream in shell side of reactor is not feasible because it can lead to operation problems. Similarly reboiler and condenser of a distillations column are set as forbidden match.



	DST-100_Cond	DST-103_Cond	DST-101_Cond	DST-102_Cond	DST-104_Cond	PBR-100	S-7
S-1	⊕	⊕	⊕	⊕	⊕	✕	⊕
DST-104_Reb	⊕	⊕	⊕	⊕	✕	✕	⊕
DST-103_Reb	⊕	✕	⊕	⊕	⊕	✕	⊕
S-20	⊕	⊕	⊕	⊕	⊕	✕	⊕
S-3	⊕	⊕	⊕	⊕	⊕	✕	⊕
DST-102_Reb	⊕	⊕	⊕	✕	⊕	✕	⊕
DST-100_Reb	✕	⊕	⊕	⊕	⊕	✕	⊕
DST-101_Reb	⊕	⊕	✕	⊕	⊕	✕	⊕

Figure 25. Forbidden matches for heat integration of toluene methylation process.

Using Aspen Energy Analyzer® design mode, 10 heat networks designs are generated. The results are shown in Table 16 with increasing total annualized cost. The best design is Design 8 which gives the minimum total cost of 6,503,761 $/yr. Figure 26 shows the grid diagram of Design 8.

From Figure 26 it can be seen that PBR-100 is only matched with HP steam Generation cold utility in accordance with the forbidden matches, in Figure 25. The remaining forbidden matches are also satisfied. Table 17 shows the detailed summary of Design 8.

Table 16. Heat Network Designs Generated by Aspen Energy Analyzer

Name	Area	Units	Shells	Capital Cost Index (*CC*)	Heating Load	Cooling Load	Operating Cost Index (*OC*)	Total Cost Index (*TAC*)
	m^2			$/yr	kW	kW	$/yr	$/yr
Design 8	9510	22	45	2,710,780	67492	69296	5,630,015	6,503,761
Design 5	10068	28	59	2,937,673	67133	68937	5,584,294	6,531,173
Design 7	9688	25	43	2,732,019	68065	69869	5,676,034	6,556,625
Design 3	10843	28	54	3,087,766	67364	69168	5,582,139	6,577,396
Design 0	8275	22	49	2,439,558	71380	73184	5,902,828	6,689,153
Design 2	8403	22	37	2,407,209	71295	73099	5,943,518	6,719,416
Design 9	7262	23	34	2,119,206	74993	76797	6,239,222	6,922,290
Design 4	7839	23	35	2,257,916	74908	76712	6,252,814	6,980,591

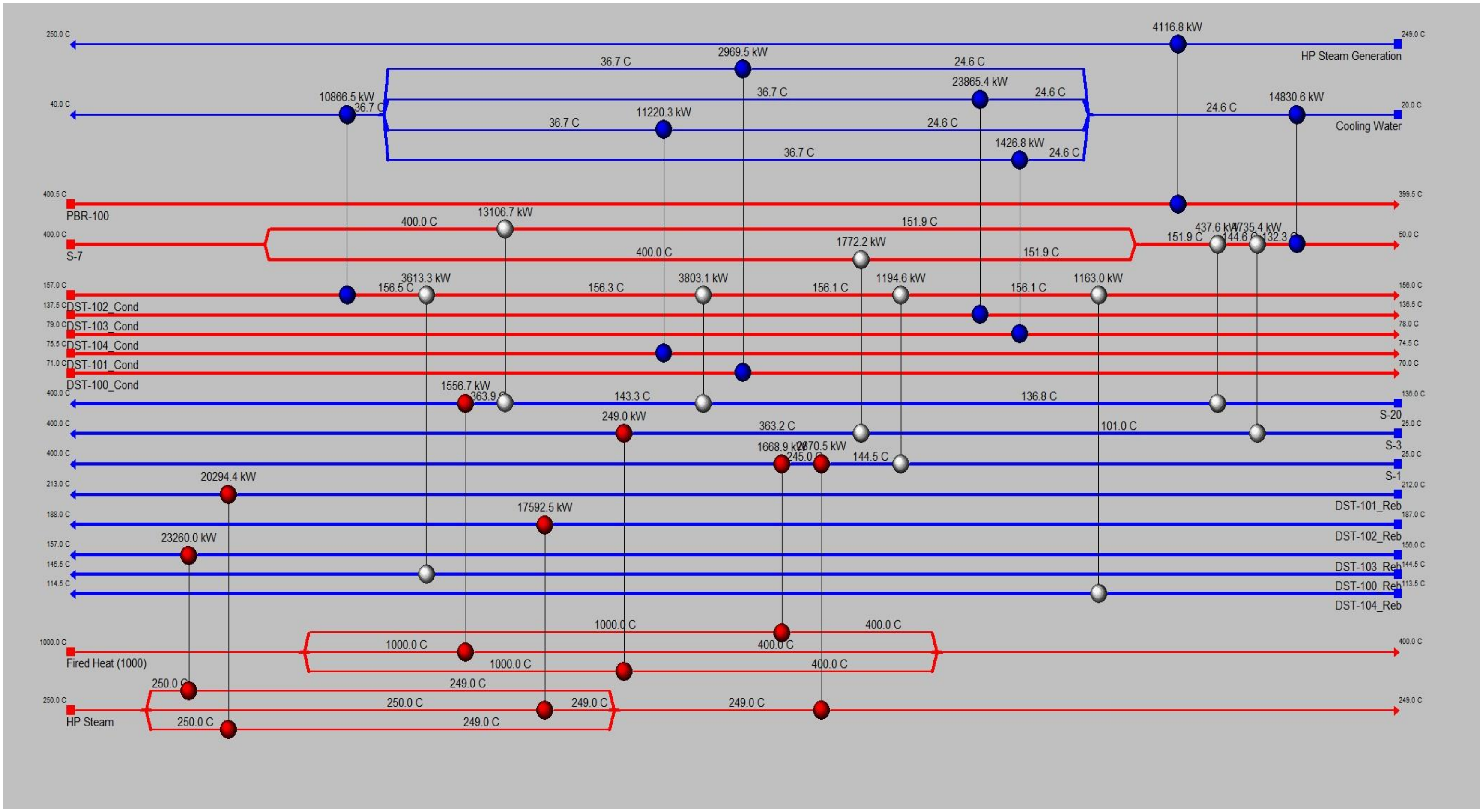


Figure 26. Gird diagram of heat network Design 8.

Table 17. Results Summary for Heat Network Design 8

Name	**Load**	**Area**	**Cost Index**	**Hot Stream**	**Hot t_{in}**	**Hot t_{out}**	**Cold Stream**	**Cold t_{in}**	**Cold t_{out}**	**ΔT Hot End**	**ΔT Cold End**
	kW	m^2	$								
E-105	1668.9	72.1	34525.5	Fired Heat (1000)	1000.0	400.0	S-1	245.0	400.0	600.0	155.0
E-106	1556.7	91.9	44206.0	Fired Heat (1000)	1000.0	400.0	S-20	363.9	400.0	600.0	36.1
E-107	249.0	14.6	17860.6	Fired Heat (1000)	1000.0	400.0	S-3	363.2	400.0	600.0	36.8
E-108	23260.0	384.2	103486.1	HP Steam	250.0	249.0	DST-103_Reb	156.0	157.0	93.0	93.0
E-109	17592.5	435.8	113406.5	HP Steam	250.0	249.0	DST-102_Reb	187.0	188.0	62.0	62.0
E-110	20294.4	842.4	211232.3	HP Steam	250.0	249.0	DST-101_Reb	212.0	213.0	37.0	37.0
E-111	10866.5	258.0	77976.7	DST-102_Cond	157.0	156.5	Cooling Water	36.7	40.0	117.0	119.8
E-112	3613.3	860.9	214756.7	DST-102_Cond	156.5	156.3	DST-100_Reb	144.5	145.5	12.0	12.8
E-113	13106.7	2052.5	587026.3	S-7	400.0	151.9	S-20	143.3	363.9	36.1	12.6
E-114	1772.2	255.4	106497.2	S-7	400.0	151.9	S-3	101.0	363.2	36.8	50.8
E-115	3803.1	1212.7	302086.1	DST-102_Cond	156.3	156.1	S-20	136.8	143.3	13.0	19.4
E-116	2870.5	123.0	47587.8	HP Steam	249.0	249.0	S-1	144.5	245.0	4.0	104.5
E-117	1194.6	94.9	40548.5	DST-102_Cond	156.1	156.1	S-1	25.0	144.5	12.6	131.1
E-118	437.6	194.6	64255.2	S-7	151.9	144.6	S-20	136.0	136.8	15.1	12.6
E-119	1163.0	108.3	43949.8	DST-102_Cond	156.1	156.0	DST-104_Reb	113.5	114.5	41.6	42.5
E-120	4735.4	420.1	110417.9	S-7	144.6	132.3	S-3	25.0	101.0	43.5	107.3
E-121	2969.5	210.9	67847.1	DST-100_Cond	71.0	70.0	Cooling Water	24.6	36.7	34.3	45.4
E-122	23865.4	631.2	169746.7	DST-103_Cond	137.5	136.5	Cooling Water	24.6	36.7	100.8	111.9
E-123	11220.3	714.9	186475.7	DST-101_Cond	75.5	74.5	Cooling Water	24.6	36.7	38.8	49.9
E-124	1426.8	84.2	37753.9	DST-104_Cond	79.0	78.0	Cooling Water	24.6	36.7	42.3	53.4
E-125	4116.8	12.0	15853.1	PBR-100	400.5	399.5	HP Steam Generation	249.0	250.0	150.5	150.5
E-126	14830.6	435.2	113284.6	S-7	132.3	50.0	Cooling Water	20.0	24.6	107.7	30.0

6.6. Second Law Analysis for Best Heat Network Design

From section 6.5 the best heat network is Design 8. The grid diagram is shown in Figure 26 and results summary given in Table 17. Second law analysis is repeated for this network design so that effect of heat integration is assessed. The procedure and assumptions mentioned in section 5.1 are used. The results are shown in Table 18.

The total $L\dot{W}$ generated in Design 8, after heat integration, is 35671.1 kW which is 23% less than the $L\dot{W}$ generated in second law analysis of section 5 (46480.6 kW). This shows that the heat integration of the process has reduced the lost work generation; however, the relative $\%L\dot{W}$ is the same.

Table 18. Second Law (Lost Work) Analysis of Heat Integration Design 8

Name of Block	Change in Stream Availability	Work	Heat Exchanger ID	Heat	Temp	Heat Equivalent of Work	Lost Work	% Lost Work
	$\Sigma\dot{A}_{in} - \Sigma\dot{A}_{out}$	$\Sigma\dot{W}_{in} - \Sigma\dot{W}_{out}$		$\dot{Q}$	t	$\Sigma\left\{\dot{Q}(1-\frac{t_o}{t})\right\}_{in} - \Sigma\left\{\dot{Q}(1-\frac{t_o}{t})\right\}_{out}$	$L\dot{W}$	$L\dot{W}$
	kW	kW		kW	°C	kW	kW	
PMP-100	-1.5	1.5					0.1	0.0
PMP-101	-1.0	1.1					0.0	0.0
PMP-102	-1.2	1.3					0.1	0.0
PMP-103	53.5	29.0					82.5	0.2
MIX-100	439.0						439.0	1.2
MIX-101	268.1						268.1	0.8
V-100	62.7						62.7	0.2
V-101	3.1						3.1	0.0
S-1	-1982.6		E-105	1668.9	400.0	929.7	546.3	1.5
			E-116	2870.5	250.0	1234.5		
			E-117	1194.6	156.0	364.6		
S-3	-1664.0		E-107	249.0	400.0	138.7	589.5	1.7
			E-114	1772.2	275.9	809.9		
			E-120	4735.4	138.4	1304.9		
S-7	11472.2		E-113	-13106.7	253.6	-5687.8	4403.9	12.3
			E-114	-1772.2	232.1	-726.4		
			E-118	-437.6	136.0	-118.7		
			E-120	-4735.4	63.0	-535.3		
S-20	-7248.4		E-106	1556.7	400.0	867.2	897.4	2.5
			E-113	13106.7	275.9	5989.7		
			E-115	3803.1	156.0	1160.9		
			E-118	437.6	148.2	128.0		
PBR-100	5300.4			-4116.8	250.0	-1770.6	3529.8	9.9
DST-100_Cond	-204.1		E-121	-2969.5	25.0	0.0	898.8	2.5
DST-100_Reb			E-112	3613.3	156.0	1103.0		
DST-101_Cond	-2445.1		E-123	-11220.3	25.0	0.0	6283.3	17.6
DST-101_Reb			E-110	20294.4	250.0	8728.3		
DST-102_Cond	761.8		E-115	-3803.1	142.0	-1071.8	7057.6	19.8
			E-117	-1194.6	84.5	-198.7		
DST-102_Reb			E-109	17592.5	250.0	7566.3		
DST-103_Cond	190.8		E-122	-23865.4	25.0	0.0	10194.7	28.6
DST-103_Reb			E-108	23260.0	250.0	10003.8		
DST-104_Cond	59.1		E-124	-1426.8	25.0	0.0	414.2	1.2
DST-104_Reb			E-119	1163.0	156.0	355.0		
						Total	**35671.1**	**100.0**

Chapter 7: Conclusion

Catalytic toluene methylation over ZSM-5 catalyst produces p-xylene along with isomers o-xylene and m-xylene. The major problem is the separation of p-xylene from its isomers o-xylene and m-xylene. These are difficult to separate due to close boiling points. By modification of the catalyst with Mg, p-xylene selectivity is improved [39]. In the process developed Mg modified ZSM-5 is used. A sensitivity analysis is made which shows that by operating the reactor at low temperature, low pressure, and low contact time the selectivity of p-xylene can be increased. The result of high p-xylene selectivity at low contact time, in present sensitivity analysis, are in agreement with experimental results reported in Sotelo et al. [39] and Breen et al. [9] . Aspen Plus® Optimization tool is used to maximize p-xylene selectivity by optimizing the reactor process parameter, results are; 400 °C temperature, 2.5 g h/mol space time and toluene-to-methanol feed ratio of 2. Toluene-to-methanol feed ratio of 2 gives a bit less conversion but significantly reduces the methanol loss to side reactions.

A process is developed using the modified catalyst and optimized reaction conditions which produce high purity p-xylene. If the recovery cost of extractive chemicals is not considered, the separation cost of p-xylene is highly reduced due to highly selective reactor and by use of reactive distillation to separate p-xylene. The process is shown in Figure 16. The product of the process is 99.7% pure p-xylene with overall 83% conversion of feed toluene to p-xylene, the rest 17% of toluene is lost to side reactions forming benzene, o-xylene and m-xylene. Due to increasing demand for p-xylene this process can be used to produce p-xylene efficiently.

Then a second law analysis is made for the process developed to highlight the areas of less thermodynamic efficiency. The major areas of lost work are heat exchangers, so heat integration of the process is done using Aspen Energy Analyzer ®. The best heat network design, which gives minimum total cost, is again evaluated showing 23% less total lost work, $L\dot{W}$, generation.

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Appendix

Table A.1. Pump Equiment Summary Report for Toluene Methylation Process

Name	PMP-100	PMP-101	PMP-102	PMP-103
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3
Specified discharge pressure [bar]	3	3	4.5	8.5
Pump efficiencies	0.85	0.85	0.85	0.85
Driver efficiencies	0.95	0.95	0.95	0.95
Fluid power [Watt]	1235.27	873.359	1017.83	23408.4
Calculated brake power [Watt]	1453.26	1027.48	1197.44	27539.3
Electricity [Watt]	1529.74	1081.56	1260.47	28988.7
Volumetric flow rate [cum/hr]	22.3831	15.8253	11.1036	115.439
Calculated discharge pressure [bar]	3	3	4.5	8.5
Calculated pressure change [bar]	1.98675	1.98675	3.3	7.3
Head developed [J/kg]	229.76	250.561	383.213	862.084
Pump efficiency used	0.85	0.85	0.85	0.85
Net work required [Watt]	1529.74	1081.56	1260.47	28988.7
Calculated discharge pressure [bar]	3	3	4.5	8.5
Calculated pressure change [bar]	1.98675	1.98675	3.3	7.3
Head developed [J/kg]	229.76	250.561	383.213	862.084
Pump efficiency used	0.85	0.85	0.85	0.85
Net work required [Watt]	1529.74	1081.56	1260.47	28988.7

Table A.2. Distillation Column Equipment Summary Report for Toluene Methylation Process

Name	DST-100	DST-101	DST-102	DST-103	DST-104
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Number of stages	10	40	37	45	10
Condenser	PARTIAL-V-L	PARTIAL-V-L	TOTAL	TOTAL	TOTAL
Reboiler	KETTLE	KETTLE	KETTLE	KETTLE	KETTLE
Number of phases	2	2	2	2	2
Top stage pressure [bar]	4	8	3	1	0.4
Specified distillate rate [kmol/hr]	128	84	802	184	5
Calculated molar reflux ratio	1.2	11.9418	2	11.861	25.1807
Calculated bottoms rate [kmol/hr]	306.82	994.284	192.284	11.2843	179
Calculated boilup rate [kmol/hr]	325.314	2661.61	1922.17	2159.75	110.377
Calculated distillate rate [kmol/hr]	128	84	802	184	5
Condenser / top stage temperature [℃]	70.866	74.2488	156.207	136.997	78.2858
Condenser / top stage pressure [bar]	4	8	3	1	0.4
Condenser / top stage heat duty [kJ/hr]	-1.07E+07	-4.04E+07	-7.43E+07	-8.59E+07	-5.14E+06
Condenser / top stage subcooled duty					
Condenser / top stage reflux rate [kmol/hr]	153.6	1003.11	1604	2182.43	125.904
Condenser / top stage free water reflux ratio					
Reboiler pressure [bar]	4.2	8.2	3.2	1.1	0.5
Reboiler temperature [℃]	145.088	212.828	187.372	156.497	113.937
Reboiler heat duty [kJ/hr]	1.30E+07	7.31E+07	6.33E+07	8.37E+07	4.19E+06
Basis for specified distillate to feed ratio	MOLE	MOLE	MOLE	MOLE	MOLE
Basis for specified bottoms to feed ratio	MOLE	MOLE	MOLE	MOLE	MOLE
Basis for specified boilup ratio	MOLE	MOLE	MOLE	MOLE	MOLE
Calculated molar boilup ratio	1.06027	2.67691	9.99652	191.393	0.616633
Calculated mass boilup ratio	1.0904	2.65227	9.99606	165.353	0.616557

Table A.3. Heater Block Equipment Summary Report for Toluene Methylation Process

Name	HX-100	HX-101	HX-102	HX-103
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Specified temperature [°C]	400	400	50	400
Calculated pressure [bar]	3	3	2.49448	3
Calculated temperature [°C]	400	400	50	400
Calculated vapor fraction	1	1	0.0307423	1
Calculated heat duty [kJ/hr]	2.06E+07	2.43E+07	-1.24E+08	6.79E+07
Net duty [kJ/hr]	2.06E+07	2.43E+07	-1.24E+08	6.79E+07