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Intensification of an Irreversible Process Using Reactive Distillation – Simulation Studies

Shuwana Tasleem[1] V. Ramesh Kumar[2]
[1,2]*University College of Technology, Osmania University, Hyderabad – 500007*

***Abstract:** In this study, a steady state simulation of the process for the production of xylene isomers by reactive distillation was performed using Aspen Plus software. The simulations were aimed studying the parameters like number of stages in the different sections of the RD column, reflux ratio, and the boil-up ratio, which maximize the conversion of Toluene and improves the selectivity and yield of the p- Xylene.*
***Keywords:** Reactive Distillation, Process Intensification, Toluene Methylation, Aspen Plus, Simulation Studies,*

I. INTRODUCTION

Reactive Distillation (RD) is a competitive technology which combines reaction and distillation in a single vessel and offers distinct advantages in terms of product selectivity and also the process economics. The principle involved is favorable manipulation of the concentration profiles in the reactive zone of the RD column to expedite the desired reaction.

The reactive distillation technique, however, has typically been applied to all the reversible chemical reactions so far, exploiting the shift in the equilibrium due to separation of one of the products. Conversely, it is very much possible to use the reactive distillation technology for the processes involving irreversible reactions.

Mohr and Sanchez [1] were the first to propose a reactive distillation process for the production of xylenes by contacting toluene with a methylating agent in the presence of a toluene methylating catalyst. The schematic of the process is shown in figure 1. In this study, an attempt is made to conduct simulation studies for the production of xylenes, essentially the para isomer from toluene methylation.

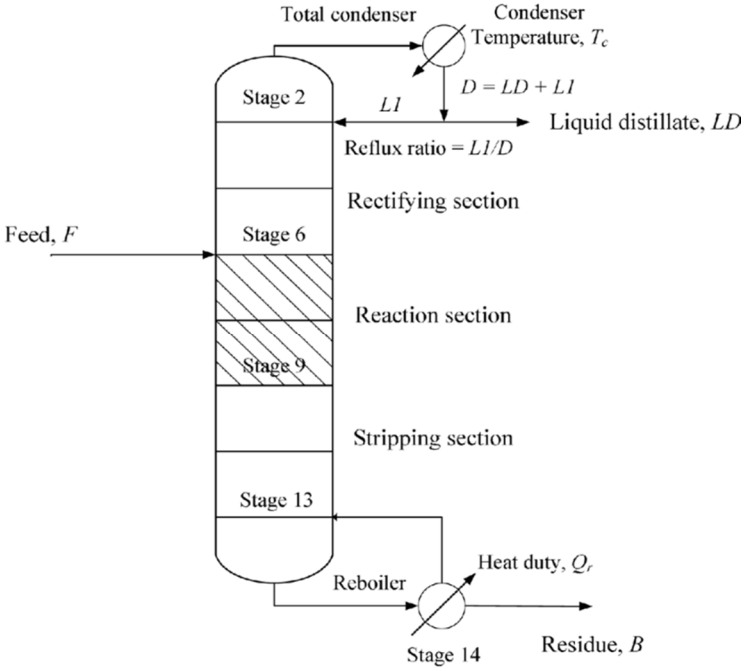

Fig. 1. The Schematic Diagram of a Reactive Distillation Column.

Xylenes, as such find varied applications, as a solvent in paints, glues and degreasing agents as it offers good solvent capacity and relatively fast evaporation. Of the xylene isomers, i.e., ortho-, meta- and paraxylene, paraxylene is the principal precursor to terephthalic acid dimethyl terephthalate , which are raw materials used in the manufacture of polyethylene terephthalate (PET) used in polyester fibers, molded plastics, films, and blown beverage bottles [2]. All the three isomers are raw materials for synthesis of special chemicals such as vitamins, pharmaceuticals, flavoring agents etc [3].

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Xylenes are also used as an ingredient in aviation fuel and gasoline. A smaller portion of the mixed xylenes produced annually are added to gasoline to improve octane ratings. A typical gasoline contains between 1 and 6% xylene [4].

Various processes are available for the production of xylenes, which include extraction from reformate by catalytic reforming [5], coal carbonization [6], dehydrocyclodimerization and methylation of light aliphatic hydrocarbons [7]. In view of the limited availability of the naturally available feedstocks and the environmental regulations with respect to the by-products obtained in the above mentioned processes, a novel process for the production of the xylenes is introduced by [1]. The invention [1] introduces a reactive distillation process for producing xylene by toluene methylation resulting in a high toluene to xylenes conversion with reduced by-product formation.

Reactive distillation is an integrated unit operation which combines the reaction vessel and the separation still into unit, providing the advantages like If RD is applied for exothermic reaction heat can be used for vaporization of liquid. This leads to savings of costs by reduction of reboiler duties.

1) The maximum temperature in reaction zone is limited to the boiling point of the mixture so that the danger of hot-spot formation in the catalyst is reduced significantly. A simple and reliable control is achieved.
2) If the reaction zone in RD column is placed above the feed point poisoning of catalyst can be avoided. This leads to longer catalyst lifetime compared to conventional systems
3) Simplification or elimination of separation system can lead to significant capital savings
4) Improved conversion of reactant. This increasing in conversion gives benefit in reduced recycle costs
5) Improved selectivity. Removing one of the products from the reaction mixture or maintaining a low conversion of one of the reagents can lead to a reduction of rates of side reactions and hence improved selectivity for a desired product
6) Significantly reduced catalyst requirement for same degree of conversion
7) Avoidance of azeotropes. RD is particularly advantageous when the reaction product is a mixture of species that can for several azeotropes with each other. RD conditions can allow azeotropes to e reacted away in a single vessel.
8) Reduced capital investment. by carrying out chemical reaction and distillation in the same vessel one process step is eliminated along with associated pumps piping and instrumentation
9) Increased speed and approved efficiency
10) Lower costs – reduced equipment use, energy use and handling
11) Less waste and fewer by-products
12) Improved product quality – chemicals are exposed to heat only once reducing opportunity for degradation

These potential benefits of the reactive distillation are however marred by the complexities encountered in the process development and design. The solution of the difficulties evolved involves enormous effort, time and cost. However, simulation studies offer a simple and a reliable ground to predict the performance of the process. There are several advantages of computer-aided simulation [8].

a) Allows the designer to quickly test the performance of synthesized process flow sheets and provide feedback to the process synthesis activities.
b) Can be coordinated with process synthesis to develop optimum integrated designs.
c) Minimizes experimental and scale-up efforts.
d) Explores process flexibility and sensitivity by answering "what-if" questions.
e) Quantitatively models the process and sheds insights on process performance.

II. TOLUENE METHYLATION SYSTEM

A. Xylenes Synthesis

The application of reactive distillation technology, for the production of xylenes offer superior process performance yielding ultra-high p-Xylene selectivity, higher total Xylenes yield, lower investment costs, reduced size of reactor and elimination of separate p-Xylene recovery unit. With numerous applications of Xylenes, the production of xylenes has increased over the recent years. p-Xylene is an essential precursor to terephthalic acid and dimethyl terephthalate, both are key components in the production of poly-ethylene terephthalate (PET). o-Xylene is used mainly in the synthesis of phthalic acid anhydride while m-xylene is usually oxidized to isophthalic acid Recently, the Xylenes are proposed to be produced toluene disproportionation. However, co-formation of benzene has made this route less viable. The alkylation of toluene is another potential route with great economic interest; where methanol can be used as the alkylating agent, which is a low-priced raw material and available in abundance [9].

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In the present reactive distillation process, the xylene isomers are produced by methylation of toluene using methanol over zeolite catalysts, preferentially ZSM-5. The xylenes formed undergo a side reaction with methanol to give trimethyl benzene. The reactions involved in the process is written as follows

$$C_6H_5CH_3 + CH_3OH \rightarrow C_6H_5(CH_3)_2 + H_2O \quad (1)$$

$$C_6H_5(CH_3)_2 + CH_3OH \rightarrow C_6H_5(CH_3)_3 + H_2O \quad (2)$$

B. Thermodynamics

Because reactive distillation is conducted under a vapor-liquid equilibrium, models suitable for liquid and vapor phases must be provided to allow simulations that closely reflect the actual situations. The non-random two-liquid (NRTL) model is used to calculate the liquid-phase activity coefficient of each component in the liquid phase. The binary parameters of NRTL for this system were determined using the steady state simulator Aspen Plus, ver 11.1.

Table 1 shows the boiling points and the azeotropic compositions from the computed result.

Table I
The Boiling Points and the Azeotropic Composition Data

S.No	Component	Boiling Point, °C	Azeotrope Data	
			Components	Composition Mole %
1	Toluene	110.68	Toluene Methanol	0.1130 0.8870
2	Methanol	64.53	Toluene Water	0.4213 0.5787
3	*p*-Xylene	138.37	*p*-Xylene Water	0.3214 0.6786
4	*o*-Xylene	144.29	*o*-Xylene Water	0.2756 0.7244
5	*m*-Xylene	139.10	*m*-Xylene Water	0.2905 0.7095
6	Water	100.02	Water TMB	0.7986 0.2014
7	1,2,3-trimethylbenzene	176.15	Methanol *o*-Xylene Water	0.1960 0.2002 0.6038

C. Reaction Kinetics

In this work, the kinetic model proposed by Rabiu and Al-Khattaf [10] is used. They [10] have studied and published the kinetics of toluene methylation over fresh and precooked ZSM-5 based catalyst in a riser simulator, which seems to be similar to a commercial fluidized bed reactor. The authors' [10] work is summarized here for a quick reference.

Based on the experimental observations, the reactions were classified based on the location of reaction

Reactions inside the pores of the catalyst

Toluene Alkylation

$$T + M \xrightarrow{k_1} P_x + H_2O \quad (3)$$
$$\xrightarrow{k_2} O_x + H_2O$$
$$\xrightarrow{k_3} M_x + H_2O$$

Internal Isomerization

$$M_x \xrightarrow{k_4} P_x \quad (4)$$

$$O_x \xrightarrow{k_5} P_x \quad (5)$$

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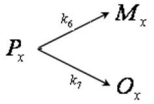
Reactions on the external surface of the catalyst

Isomerization on the catalyst surface



(6)

Xylene Alkylation to give TMB

$$M_x + O_x + P_x \xrightarrow{k_8} TMB + H_2O \quad (7)$$

Arrhenius equation $$k_i = A_i e^{-E_i / RT} \quad (8)$$

The estimated model parameters are given in Table II.

Table II
Estimated Model Parameters

i	E/kJ.mol^{-1}	$A_o \times 10^4$ / m^3/kg$_{cat}$ - sec
1	56.83	0.1435
2	67.11	0.0298
3	79.42	0.088
4	31.5	0.3590
5	32	0.6975
6	25.16	0.0070
7	25.24	0.0086
8	24.49	8.8721
α	0.001	

The kinetic parameters obtained using equation 8 were re-parameterized to reduce the parameter interaction between pre-exponential factors (A_i) and activation energies (E_i). The re-parameterization was done centering the temperature at an average reaction temperature of T_o.

Whence, k_i is then expressed as

$$k_i = k_o \exp\left[\frac{-E_i}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)\right] \quad (9)$$

The kinetic data summary is as follows

Table III
Kinetic Data, As Implemented For The Simulation In The Aspen Plus Software

S. No	E_i/R (K)	k_o at T_o = 412.5 °C
1	6835.46	0.0672
2	80.71.93	0.0023
3	9552.56	0.0008
4	3788.79	14.2973
5	3848.93	25.4455
6	3026.22	0.0848
7	3035.84	1.0270
8	2945.63	1208.5

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III. COLUMN CONFIGURATION

The process is carried out in a 50 stage reactive distillation column in which the reactant toluene and the methylating agent methanol are continuously fed to the column and the produced xylenes are continuously withdrawn from the bottom of the column. Toluene is fed on the stage above catalyst and methanol is introduced on stage below catalyst.

Toluene serves as both reactant and the heat sink. The heat of reaction produced is taken up by toluene, which flows down in the column and in utilized for vaporization. As a result the reaction zone is maintained under near isothermal conditions. Excess toluene flowing through the stripping section is separated from the xylenes and is returned to the reaction zone as vapor. Excess toluene in the enriching section passes to condenser, condenses and is refluxed back into the column. The reaction zone temperature is maintained around 190 ºC and the operating pressure for the column is 725.7 kPa. The molar ratio of toluene to methanol is to be greater than 1 and, more preferably greater than 10.

A. Reactive Distillation Model

Simulation model for the transalkylation of toluene in reactive distillation is build using the commercially available ASPEN PLUS simulation package, version 11.1. The built-in RADFRAC model was chosen to simulate the process. The model required the specifications of the components, reaction kinetics, feed conditions, operating conditions, column configuration and two operating parameters (reboiler duty/condenser duty/reflux rate/reflux ratio/distillate rate/bottoms rate) to generate simulation results. The NRTL model was used for the liquid phase activities. The SRK equation of state was used for fugacity coefficients, enthalpy and other properties. The reaction rate expressions given by equations 1 to 8 were used for kinetic modeling.

The schematic of the column with preliminary configuration is shown in Fig. 2.

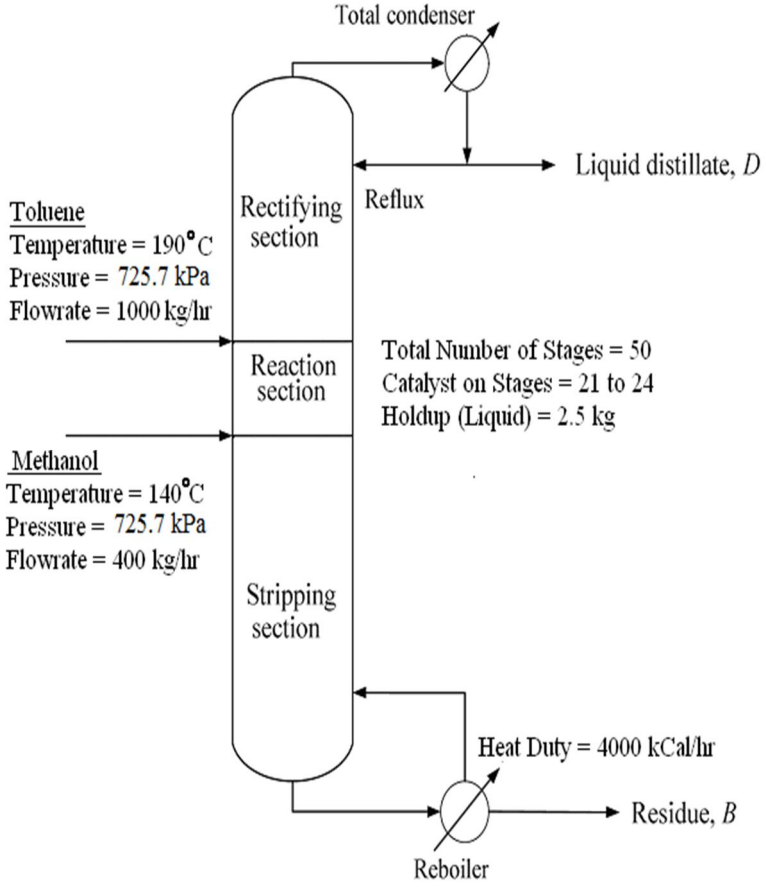

Fig. 2. The configuration of a reactive distillation column for Toluene Methylation Process

The column contains total 50 stages counted from top to bottom; the catalyst placed between stages 21-24. The stages 1-20 constitutes rectifying section and stages 25-50 makes up the stripping section.

The ASPEN PLUS model of the column is shown in figure 3. Column specifications and feed conditions for the preliminary configuration are summarized in table 5.

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Table IV
Preliminary Feed Conditions and Column Configuration for Toluene Methylation

Feed Conditions			Column Configuration	
Quantity	Toluene	Methanol		
Flowrate, kg/hr	1000	400	Total Number of Stages	50
Temperature, ºC	190	140	Rectification stages	20
Pressure, kPa	725.7	725.7	Reaction stages	5
Phase	Liquid	Vapor	Stripping Stages	25
Feed Stage	20	25	Catalyst Wt, kg	2.5 kg per stage
Mole Fraction	1.0	1.0	Reflux Ratio	1.2
			Column Pressure, kPa	725.7
			Reboiler Duty, kCal/hr	4000

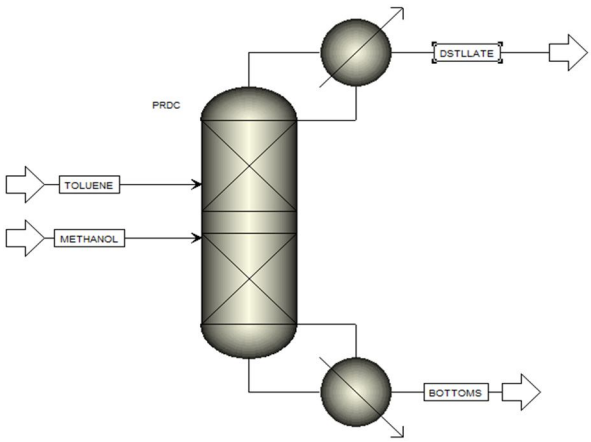

Fig. 3. The Aspen Plus Flow sheet for the simulation of Toluene Methylation Process

IV. RESULTS AND DISCUSSION

The products obtained in the preliminary run using configuration given in Table 4 is shown in Table 5

Table V
Results of base case simulation

Component	Distillate		Residue	
	kmol/hr	kg/hr	kmol/hr	kg/hr
Toluene	0.0003	0.02784	5.35982	493.857
Methanol	5.11753	163.977	1.87316	60.0201
p-Xylene	0.00018	0.01878	5.00985	531.883
o-Xylene	5.54E-24	5.9E-22	0.42347	44.9582
m-Xylene	3.73E-05	0.00396	0.05933	6.29901
Water	1.56E-05	0.00028	5.49285	98.9552
Trimethyl Benzene	0	0	1.89E-23	2.3E-21

From Table V it can be inferred that the column top product consists mainly the un-reacted raw materials and water along with traces of xylene isomer. The desired product, p-xylene amounting to a mole fraction of 0.275 is found in bottoms product. The undesired trimethyl benzene, likely to be formed as the product of xylene methylation is found in minute traces less than a fraction of order 3.7×10^{-24}. Therefore, considered zero in the products.

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The performance of the reactive distillation column is evaluated in terms of conversion of Toluene, selectivity of p-Xylene and the p-Xylene to o-Xylene ratio. These quantities are defined as follows

$$Conversion\ of\ Toluene\ = \frac{Difference\ in\ molar\ \ flowrate\ of\ \ inlet\ and\ outlet\ of\ \ Toluene}{Feed\ molar\ \ flowrate\ of\ \ Toluene} \times\ 100\ \%$$

$$Selectivity\ \ of\ p\ =\ Xylene\ \ =\ \frac{molar\ flowrate\ of\ p-Xylene\ in\ Residue}{Total\ molar\ flowrate\ of\ all\ Xylene\ isomers\ in\ Distillate\ and\ in\ Residue}$$

For the preliminary configuration, the conversion of toluene is found to be 50.61 % and the selectivity of p-Xylene is 0.9121. 46.2 % of p-Xylene yield was obtained with p-Xylene to o-Xylene ratio of 11.83.

B. Sensitivity Analysis

The sensitivity of the process was analyzed for the following parameters

1) Design Variables

Total Number of Stages

a) Rectifying stages
b) Reaction stages
c) Stripping stages

2) Operating Variables

a) Reflux ratio
b) Boil-up ratio

3) Effect of Number of Rectifying Stage: The number of rectifying stages influence both the conversion of the Toluene as well as the selectivity of the p-Xylene. The conversion of the Toluene initially increases with the increase in the rectifying stages upto 6 stages and after that, it remains essentially constant; however the selectivity of p-xylene is high with least number of rectifying stages and decreases with an increase in number of stages. The result of this simulation is shown in Fig. 4. Based on these results, an optimum number of 6 stages are chosen in the rectification section.

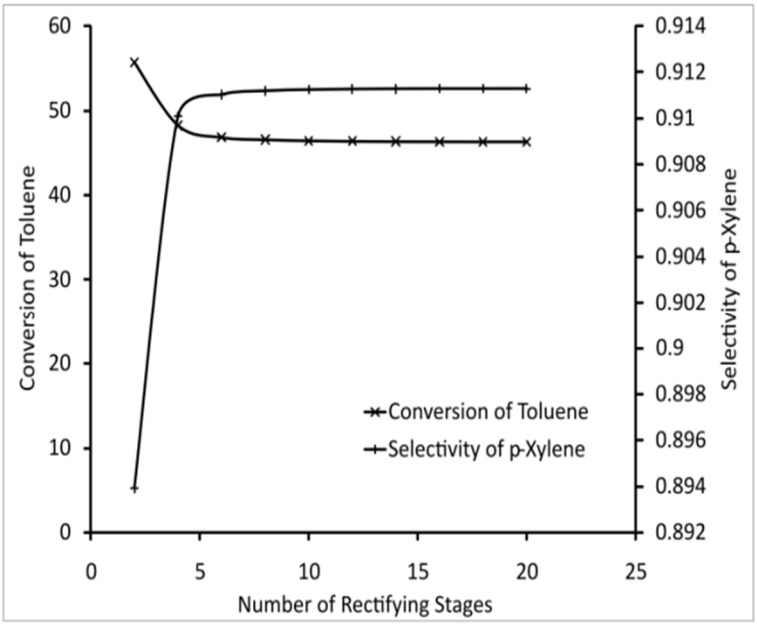

Fig. 4. Effect of the number of stages in the rectification section of the RD column

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4) *Effect of Number of Reaction Stages:* 8 Reaction stages were chosen as optimum number of stages; as the conversion was found to increase with the increasing number of stages in the reaction section. Though the graph shown in Fig. 5 indicates a maximum for selectivity of p-Xylene; the changes are not significant numerically.

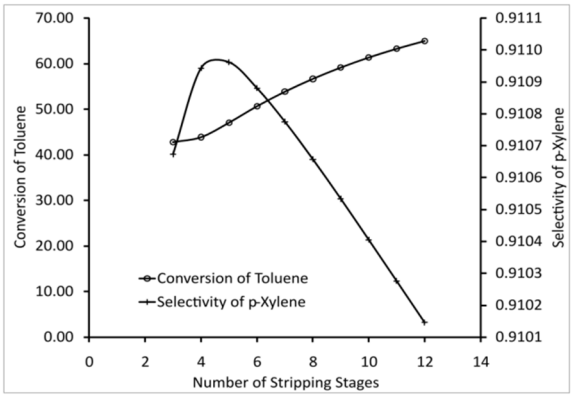

Fig. 5. Effect of the number of stages in the reaction section of the RD column

5) *Effect of Number of Stripping Stage:* Number of Stripping Stages was found t have very insignificant effect on both the conversion of Toluene as well as the selectivity of the –Xylene; however sufficient number of stripping stages as required in order to separate the low boiling un-reacted raw materials and the bye products from the xylene isomers, whence a total of 11 stripping stages were evaluated to be optimum.

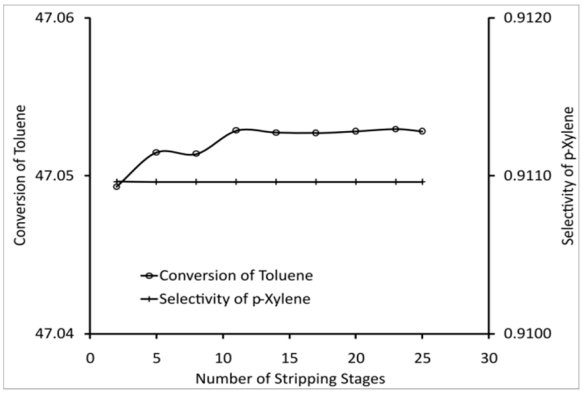

Fig. 6. Effect of the number of stages in the stripping section of the RD column

6) *Effect of Variation in Reflux ratio:* The selectivity of p-Xylene is not much effected by the increase in reflux ratio, however the toluene conversion shows significant increase, from 50 % to 65 % when the reflux ratio increased from 1 to 3.8; further increase in reflux ratio showed < 1 % increase in the toluene conversion. Therefore, a reflux ratio of 3.8 can be chosen as optimum reflux ratio. These variations in conversion of Toluene and selectivity of p-Xylene with respect to increase in reflux ratio is shown in Fig. 7.

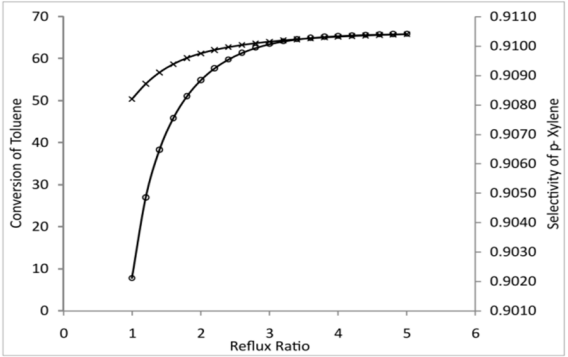

Fig. 7. Effect of the varying reflux ratio

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7) *Effect of Variation in Boil-up Ratio:* The effect of variation in boil-up ratio on the parameters under study is shown in Fig. 8. The conversion of Toluene goes through a minimum at 1 and then increases upto a boil-up ratio of 2.25 and then decreases with further increase. The selectivity of the p-Xylene also shows a similar effect at those two values of boil-up ratio. This happens because the boil-up rate is increased by increasing the reboiler duty, which in turn affects the temperature profile in the column, which influences the reaction kinetics. The initial reboiler duty of 4000 kCal/hr is found to be best, as the boil-up ratio of 2.25 would require a supply of 91000 k Cal/hr of heat. Such huge quantity of heat will effect the process economically.

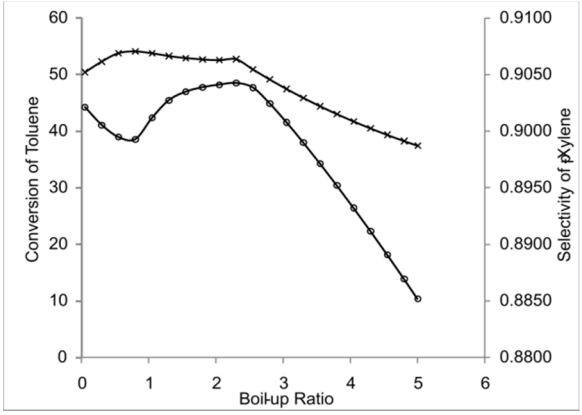

Fig. 8. Effect of the varying boil-up ratio

The optimized column was run and the following composition of the products were obtained, shown in Table 6.

Table VI
Results of Simulation of Optimized Column

Component	Distillate		Residue	
	kmol/hr	kg/hr	kmol/hr	kg/hr
Toluene	1.82	168.07	0.0247	2.28
Methanol	0.02	0.50	3.46	110.98
p-Xylene	0.00	0.02	8.1807	868.52
o-Xylene	0.0000	0.00	0.7227	76.73
m-Xylene	0.0000	0.00	0.1007	10.70
Water	6.03	108.58	2.9771	53.63
Trimethyl Benzene	0	0	3.7644E-29	4.52E-27

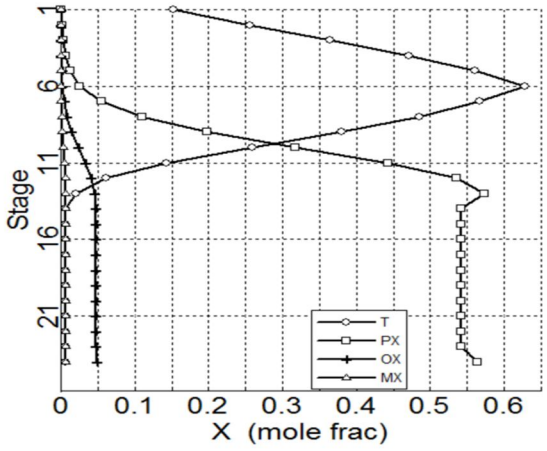

Fig. 9. Liquid composition profile of the Toluene and the Xylene isomers along the height of the optimized RD column

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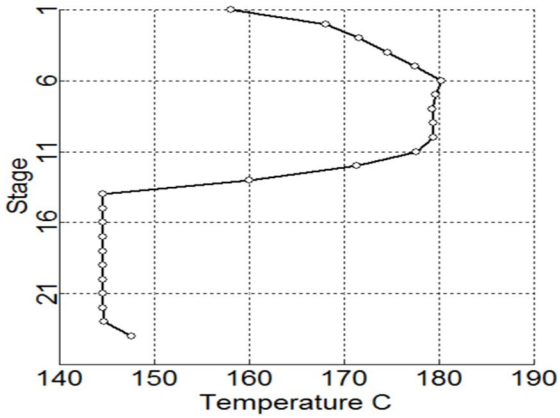

Fig. 10. Temperature profile in the optimized RD column

Fig. 9. Shows the composition profiles of the Toluene and the Xylene isomers in the liquid stream along the height of the column. The Toluene concentration is highest at the stage 6, where the fresh Toluene is introduced as feed. Tolune concentration decreases as it undergoes reaction and the un-reacted Toluene moves up the column and is removed in the distillate. As the reactions proceed, the Xylene isomers as formed the concentration in the bottom section of the column increases. Trace amount of p-Xylene goes into distillate and the other two isomers are essentially in the bottom product.

The temperature profile along the RD column is shown in Fig. 10. Unlike the typical distillation column, the temperature profile in this RD column is higher in the reactive and the rectifying sections, as compared to the stripping section. The reason being that, the reactions are exothermic, and this liberation of heat maintains the required temperature in the reaction section. The vapors carried up from this section raises the temperature of the rectifying section. Introduction of Methanol at a lower temperature helps to maintain the temperature of the stripping section less than the boiling points of Xylene isomers and this aids in the separation of the Xylenes into the bottom product.

The temperature profile along the RD column is shown in Fig. 10. Unlike the typical distillation column, the temperature profile

V. CONCLUSIONS

Simulation studies were performed using Aspen Plus software to study and optimize the reactive distillation column for the selective production of p-Xylene. The results corroborate that the process is considerably sensitive to the design and operating variables. The influence of the above mentioned parameters was evaluated in terms of the conversion of Toluene and the selectivity of p-Xylene. A total of 29 stages with 6 rectifying, 12 reactive and 11 stripping stages were found to be optimum. An increase of reflux ratio from 1.2 to 3.4 improved the process vastly and even though the increase in reboiler duty pointed that the conversion of Toluene would improve but in view utility expenses, the base case value of 4000 kCal/hr deemed better. With the optimized column configuration, the conversion of toluene improved to 83 %, the selectivity of p-Xylene was not much changed and remained to be 0.91. Conversely, the yield of the p-Xylene increased from 46 % to 75% and the mole fraction of p-Xylene in the bottom product increased from 0.275 to 0.53, indicating a product richer in p-Xylene.

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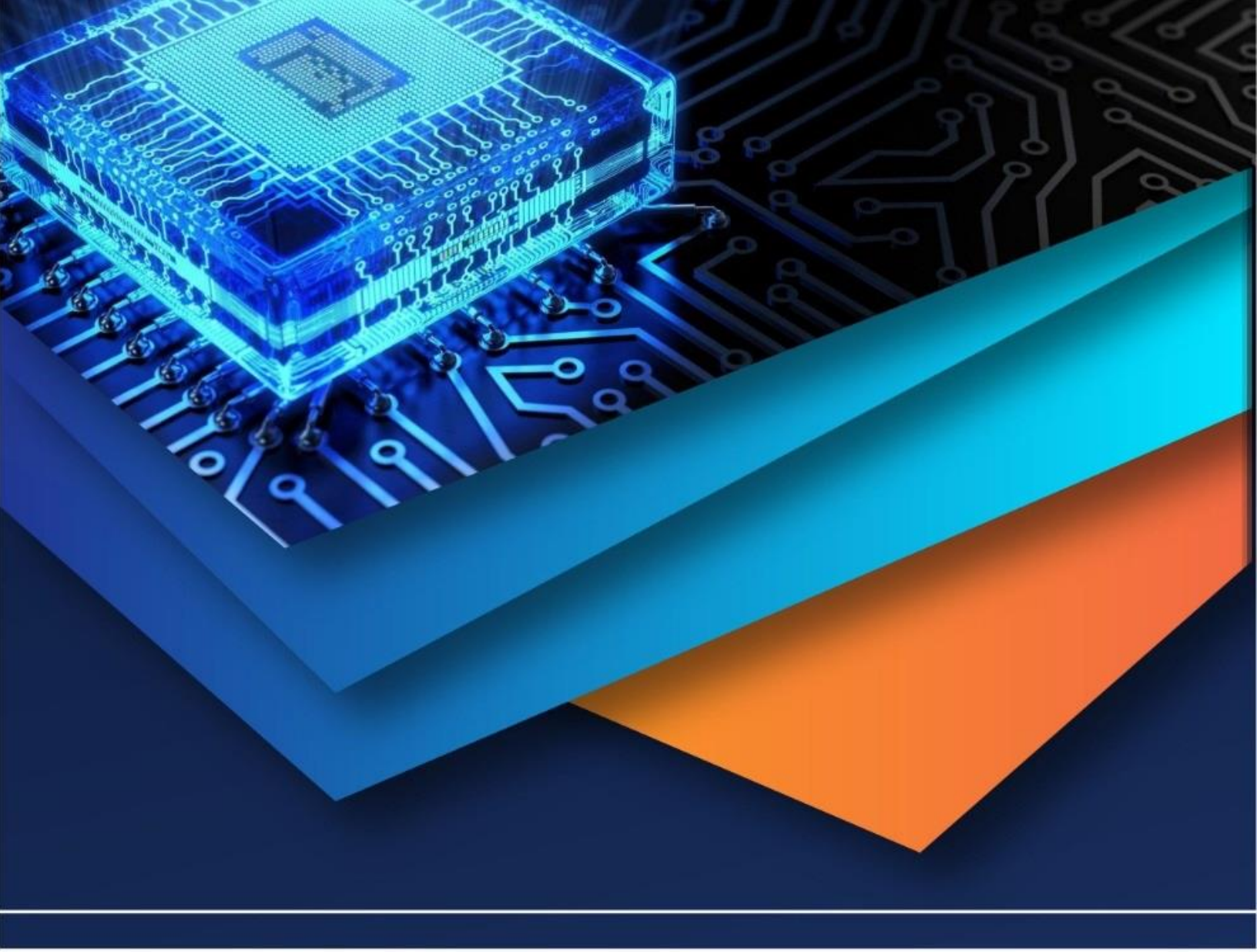

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