iJRASET
International Journal For Research in Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 9 **Issue:** XI **Month of publication:** November 2021

DOI: https://doi.org/10.22214/ijraset.2021.39104

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International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 7.429
Volume 9 Issue XI Nov 2021- Available at www.ijraset.com

Intensification of an Irreversible Process using Reactive Distillation– Feasibility Studies by Residue Curve Mapping

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Abstract: ***Reactive distillation processes are very promising in substituting Sconventional liquid phase reaction processes. However this technology is not suitable for all kind of processes or types of reaction. Therefore, assessing the feasibility of these process concepts forms an important area in current and future research and development activities. The present paper focuses on the feasibility studies based on the construction of residue curve maps for the toluene methylation system. The RCMs were constructed and analyzed; it is concluded that the process of synthesis of xylenes when carried out in the reactive distillation column enhances the selectivity of the desired para isomer.***

Keywords: Reactive Distillation, Residue Curve Maps, Feasibility Study, Toluene Methylation, Aspen Plus

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 feasibility studies for the production of xylenes, essentially the para isomer from toluene methylation.

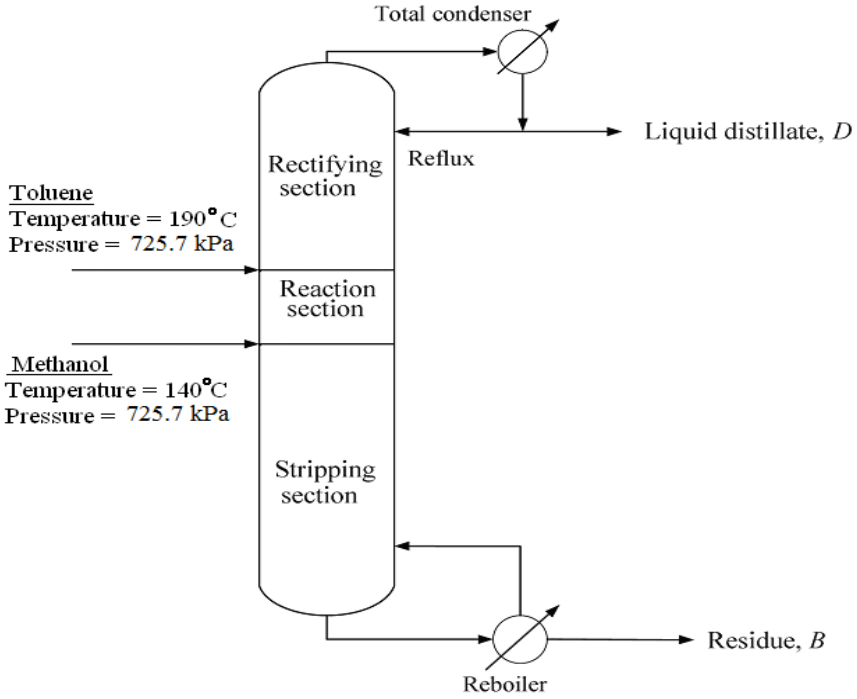

Figure 1. Schematic Diagram of the Reactive Distillation Process for the Production of Xylenes

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II. TOLUENE METHYLATION SYSTEM

A. Xylenes Synthesis

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

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

$C_6H_5(CH_3)_2 + CH_3OH \rightarrow C_6H_5(CH_3)_3 + H_2O$ 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 1shows the boiling points and the azeotropic compositions from the computed result.

Table 1.The Boiling Points Data

S.No	Component	Boiling Point, °C
1	Toluene	110.68
2	Methanol	64.53
3	p-Xylene	138.37
4	o-Xylene	144.29
5	m-Xylene	139.10
6	Water	100.02
7	1,2,3-trimethylbenzene	176.15

C. Reaction Kinetics

In this work, the kinetic model proposed by Rabiu and Al-Khattaf [2] is used. The reactions involved are summarized as below. The reaction kinetics of the system are recapitulated in our previous paper [3]

Reactions inside the pores of the catalyst

Toluene Alkylation

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

Internal Isomerization

$$M_x \xrightarrow{k_4} P_x \qquad 4$$

$$O_x \xrightarrow{k_5} P_x \qquad 5$$

Reactions on the external surface of the catalyst

Isomerization on the catalyst surface

$$P_x \xrightarrow{k_6} M_x \quad P_x \xrightarrow{k_7} O_x \qquad 6$$

Xylene Alkylation to give TMB

$$M_x + O_x + P_x \xrightarrow{k_8} TMB + H_2O \qquad 7$$

Arrhenius equation

$$k_i = A_i e^{-E_i/RT} \qquad 8$$

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III. RESIDUE CURVE MAPS

The residue curve mapping technique (RCM) is considered as powerful tool for the flow-sheet development and preliminary design of conventional multi-component separation processes. It is a basic tool for the distillation processes to get insights on the process behavior and feasibility and represents the basis for any analysis. The usefulness of residue curves in distillation analysis derives from matching a residue curve segment with the composition profile of a packed distillation column at total reflux. This property made the residue curve maps (RCMs) a useful tool to determine the separation feasibility of various multi-component systems, ideal and non-ideal azeotropic mixtures with or without reactions, in chemical equilibrium and kinetically controlled .

A. Non-Reactive RCM

In the non-reactive case no reaction takes place which implies that the composition of the liquid only depends on the composition of the vapor flow leaving the still. Therefore, only a thermodynamic model is needed to describe the composition of the vapor which is in equilibrium with the liquid.

B. Reactive RCM

The introduction of a chemical reaction into the batch distillation experiment makes that the change of the composition of the liquid is more complex. Not only the thermodynamics have to be considered, but also the kinetic effect induced by the chemical reaction. The modeling of the reactive residue curve maps can be done based on two different approaches. The first approach is to assume that the rate of reaction is infinitely fast which makes that the whole system is at chemical equilibrium at any instant in time. A second approach is to include the reaction kinetics into the RCM model to simulate the case where the process is kinetically controlled [4].

IV. RESULTS AND DISCUSSION

A. RCM for the Toluene Methylation Systems

The RCMs can be constructed theoretically using appropriate thermodynamic model. In the present study, ASPEN PLUS simulation software is used to generate the RCMs for the non-reactive mixtures. The reactive RCMs are generated using the program developed by Shakoor [5]

1) *Non-Reactive RCMs:* The Toluene methylation system consists of 7 components undergoing 8 chemical reactions. The non-reactive RCMs are obtained using NRTL model. The resulting residue curves are shown in a 3-dimensional composition space in figures 2-7., where each vertex resembles a pure component of the system. Figures 2-7 shows that besides the pure components, the system contains five singular points. The system consists of 2 stable nodes, pure components Water and 1,2,3-Trimethylbenzene; 1 unstable nodes for Toluene-Methanol azeotrope and 11 saddle points corresponding to the azeotropes formed. The compositions and temperatures of all azeotropes are given in Table 4. The non-reactive RCMs for different ternary mixtures of the present system are given in figures 2 to 7.

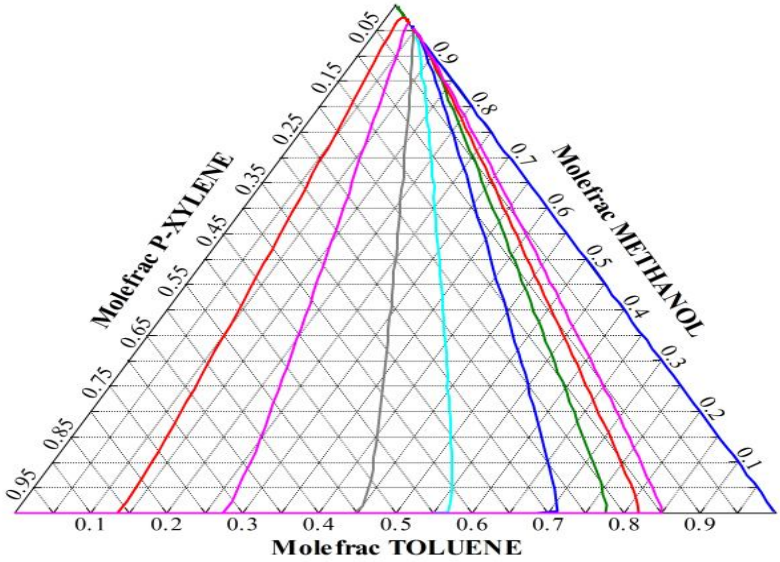

Fig. 2. Residue Curve map for Toluene/Methanol/p-Xylene

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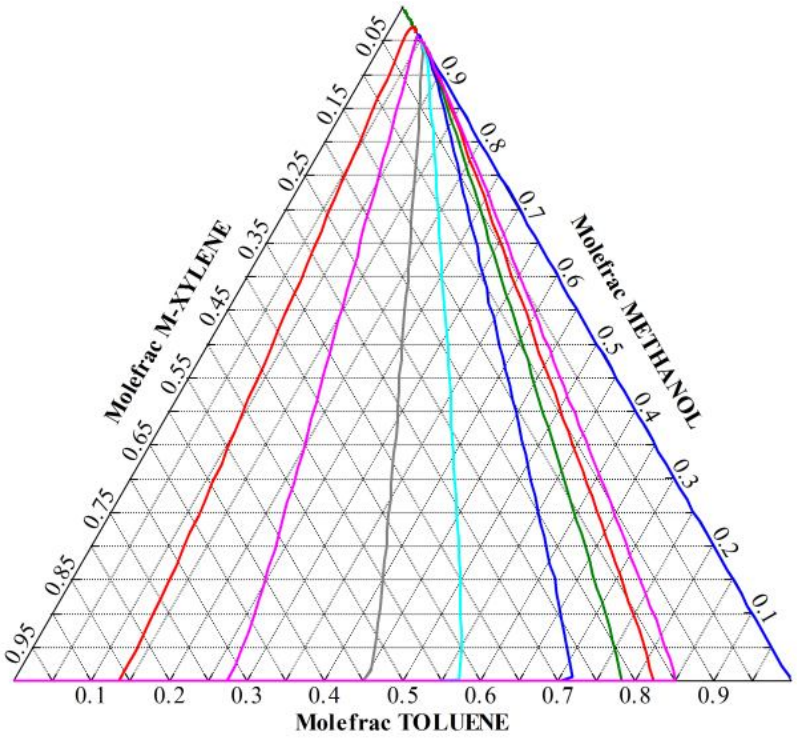

Fig. 3. Residue Curve map for Toluene/Methanol/m-Xylene

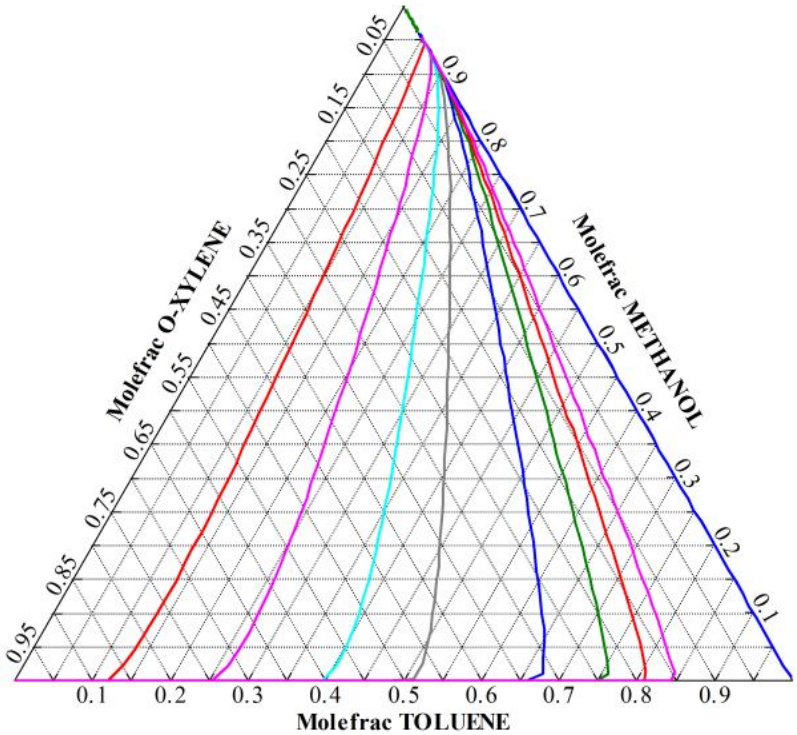

Fig. 4. Residue Curve map for Toluene/Methanol/o-Xylene

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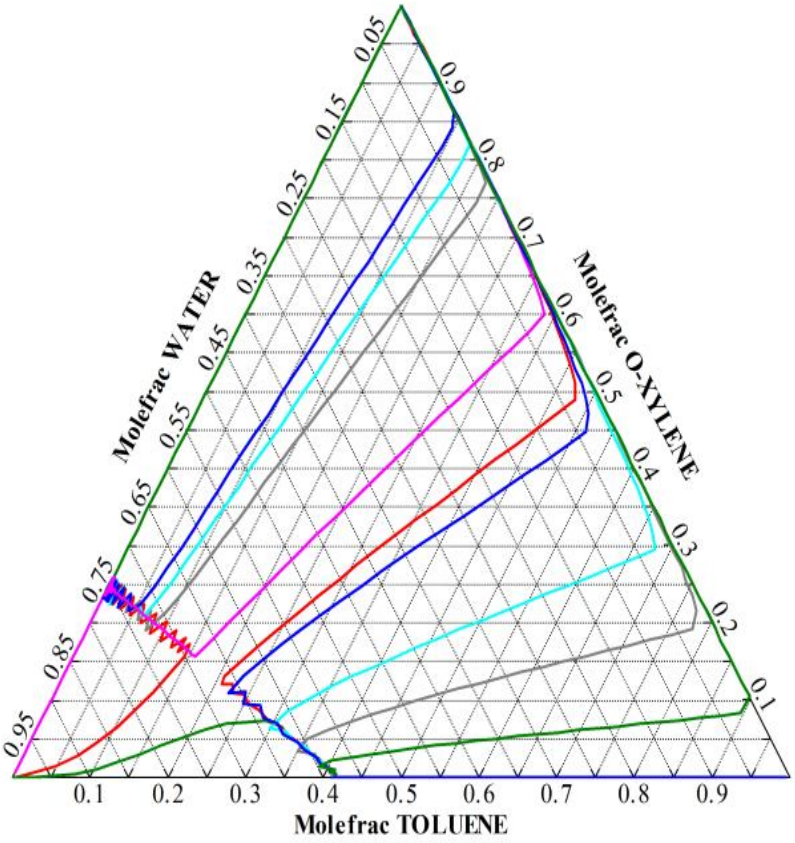

Fig. 5. Residue Curve map for Toluene/o-Xylene/Water

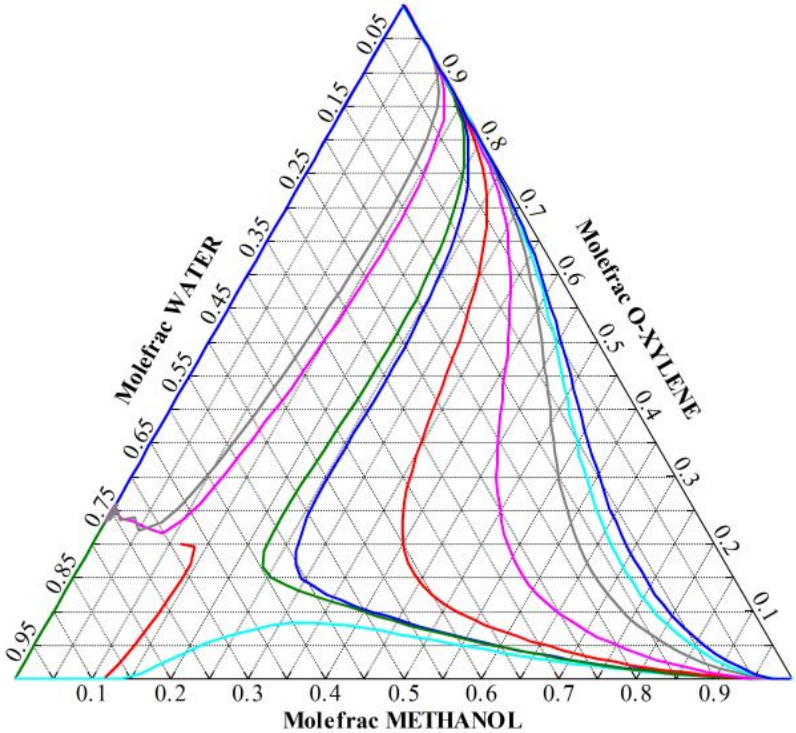

Fig. 6. Residue Curve map for Methanol/o-Xylene/Water

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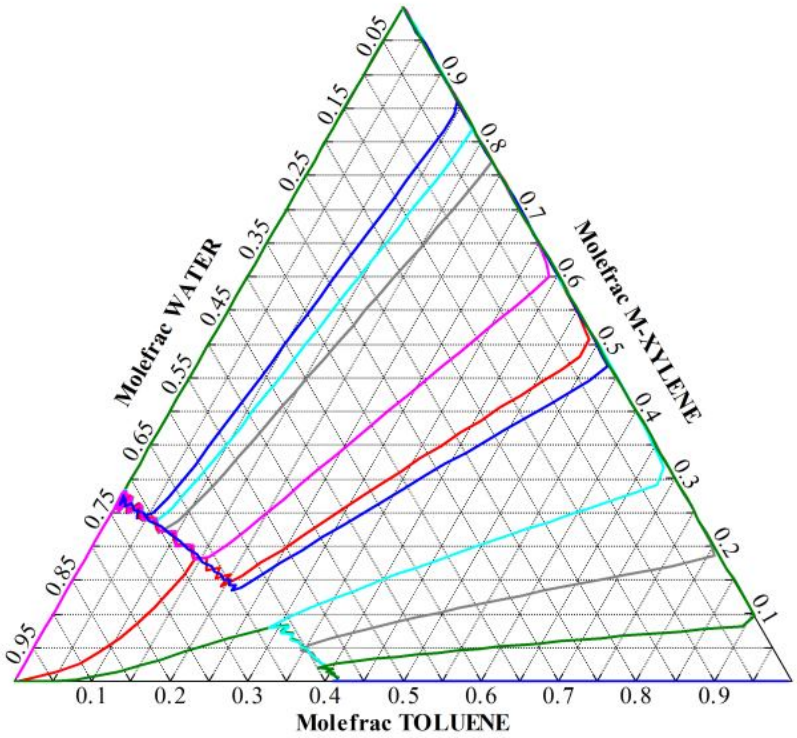

Fig. 7. Residue Curve map for Toluene/m-Xylene/Water

Table 4. Azeotropic Data at a pressure of 725.7 KPA

S. No	Temperature, °C	Mole Fraction							Type	Stability
		Toluene	Methanol	p-Xylene	o-Xylene	m-Xylene	Water	TMB		
1	124.57	0.0414	0.9586						Node	Unstable
2	141.36	0.4197					0.5803		Saddle	
3	143.51	0.1694			0.1484		0.6822		Saddle	
4	143.50	0.1609	0.0031		0.1524		0.6836		Saddle	
5	142.21	0.2410				0.1213	0.6377		Saddle	
6	145.05	0.1287					0.7089	0.1624	Saddle	
7	134.46			0.3264			0.6736		Saddle	
8	142.31				0.2462		0.7538		Saddle	
9	145.29		0.1753		0.1773		0.6474		Saddle	
10	140.02					0.2701	0.7299		Saddle	
11	144.28						0.7642	0.2358	Saddle	
12	147.59		0.1688				0.6796	0.1517	Saddle	

2) Reactive RCM: Chemical reactions can influence residue curve maps in some important ways. Reactions can lead to the disappearance of some azeotropes that exist in the absence of reaction also chemical reactions can also lead to the creation new azeotropes that would not exist in the absence of reaction [5]. The influence of reaction kinetics on chemical phase equilibrium and reactive azeotrope was investigated first by Venimadhavan et al [6] **}**, and the equations used to compute the reactive residue curves are:

$$\frac{dx_i}{d\xi} = (x_i - y_i) + \frac{Da}{k_{ref}}\left[\sum_{j=1}^{m}(v_{i,j}r_j) - x_i\sum_{i=1}^{N}\sum_{j=1}^{M}(v_{i,j}r_j)\right]$$

10

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Where Da is the Damkohler number, defined by equation 11.

$$Da = \frac{\rho V_{cat}}{V^{o}} k_{ref} \qquad 11$$

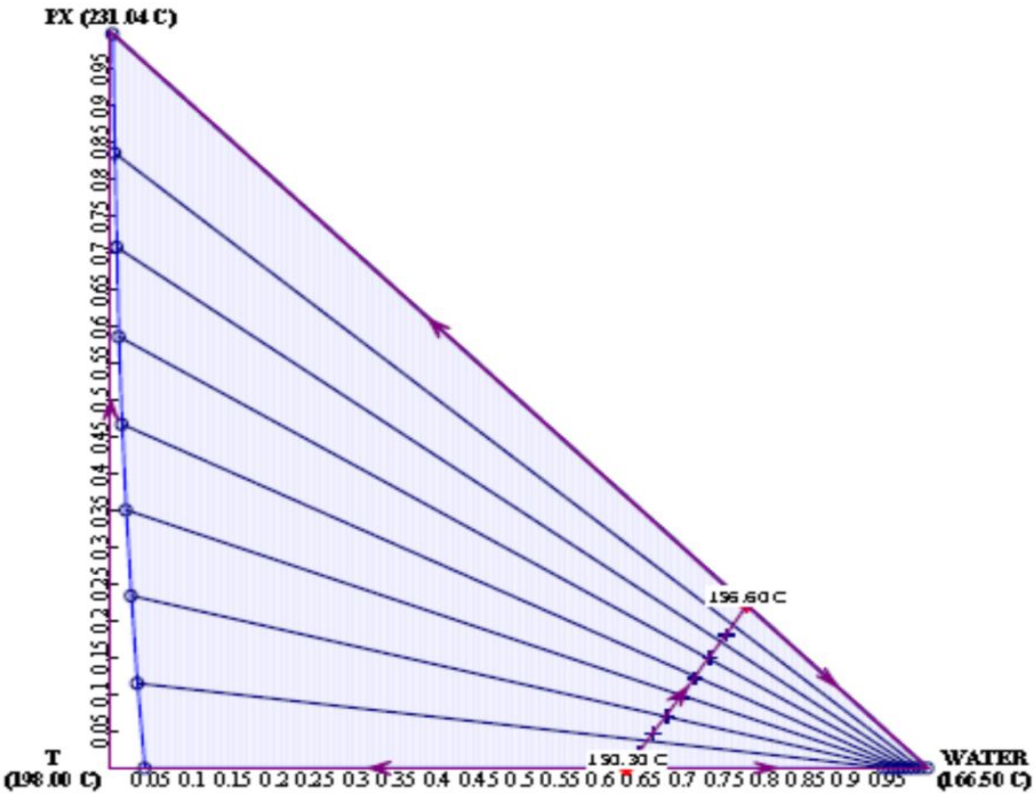

Fig. 8. Reactive Residue Curve map for Toluene/Water/*p*-Xylene for Damkohler No. 0.01

Fig. 8 shows the reactive residue curve map for the toluene methylation system at 725.7 kPa and Damkohler No. of 0.01. it shows 2 stable nodes each for the 100% of Water and *p*-Xylene and 2 unstable nodes; one at 65%water + 35% Toluene and another at 78% water + 22% *p*-Xylene. The change in azeotropic compositions and the instability shift can be attributed to the interaction between thermodynamic equilibrium and the reaction.

V. CONCLUSIONS

Residue curve map is a powerful tool to study the non-ideal distillation columns. However, the RCM technique requires accurate thermodynamic data in order to correctly describe reactive distillation processes. For the toluene methylation, the constructed RCMs predict the shift in azeotropes formed in the system; which indicate that the reactive distillation process when applied to the production of xylenes will enhance the selectivity of the desired para isomer.

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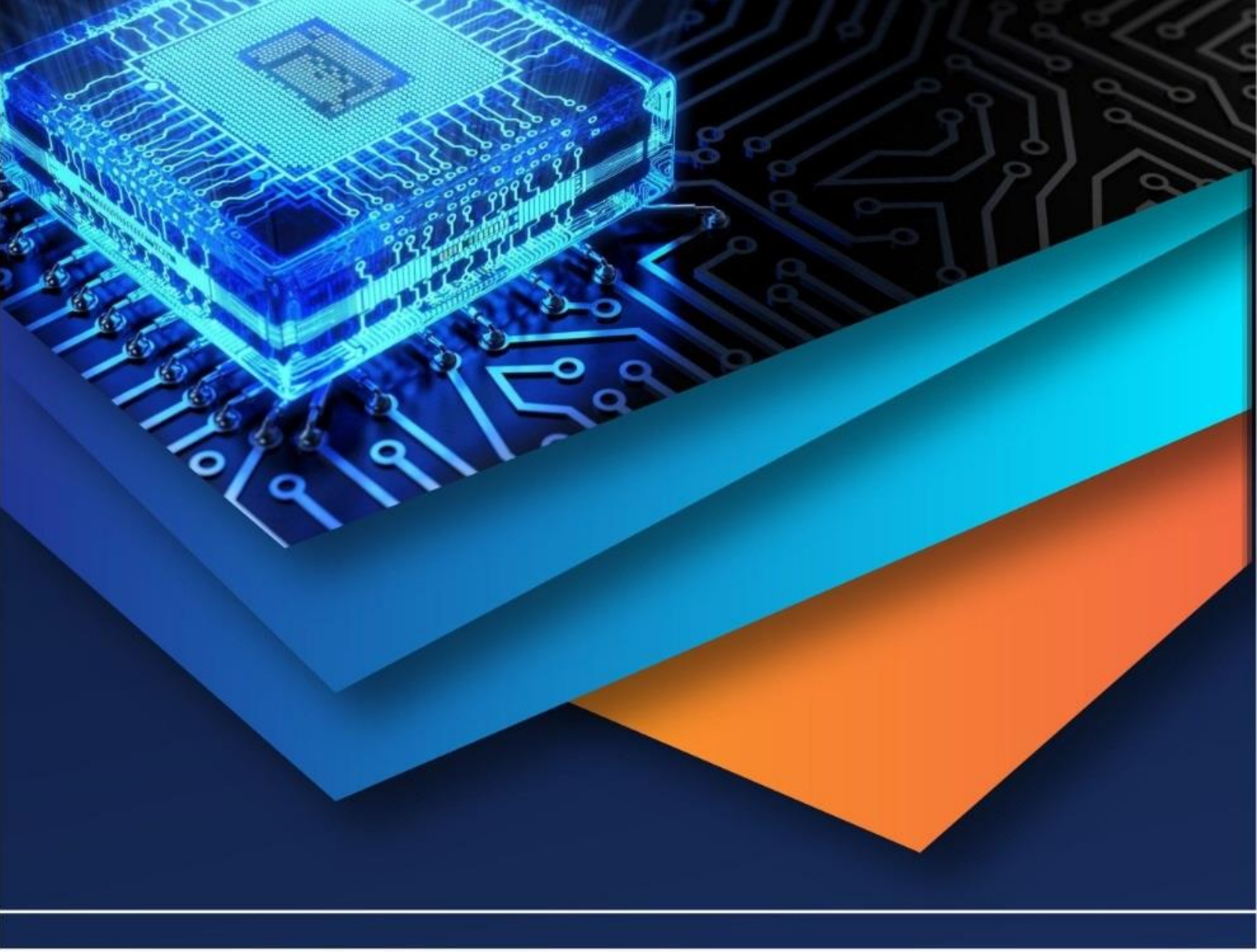

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