Overcome the equilibrium limitation in para-Xylene production by using reactive distillation method

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Abstract. To overcome the equilibrium limitation of liquid phase-Xylene isomerization in maximum para-Xylene (PX) yield at 24% molar is a significant objective in either academics or industrial application, regarding the importance of PX in various polyester productions. In this study, integration of reaction and extractive distillation into a reactive distillation column (RDC) is proposed as a solution for the enhancement of PX yield. The desired product is simultaneously generated and purified in the only equipment so the conversion could be forward shifted to overcome equilibrium limitation in Xylene isomerization. Obstacles relating to the close boiling points of xylenes are alleviated by an inert solvent introduced into the system to facilitate the separation of xylene isomers. The flowsheet which is configured by a reactive distillation column and a recovery column manifests advantages of the method for para-Xylene production. The highest PX yield can be obtained up to 37% molar, while other cases result in the yield of p-Xylene higher than 25% molar. The effect of design parameters, including the number of stages in reactive-, rectifying- and stripping sections on process performance, is carefully examined to study the behavior of the RDC and system.

Keywords: para-xylene, reactive distillation, isomerization, equilibrium.

1. Introduction

Para-xylene (p-Xylene or PX) is an important immediate which is mostly used for the synthesis of PET (Poly Ethylene tere-Phthalate) resin and fiber productions. The production of p-Xylene has been investigated into the gas phase if the feed contains Ethylbenzene [1, 2] or liquid phase in the free basic of Ethylbenzene presence [3-5]. For instance, Xylene liquid-phase isomerization is a promising conversion for PX production but it is limited by equilibrium barrier which draws the maximum yield of para-Xylene at 22-24%. To adapt to the increasing demand for PX in industry, however, this amount is not sufficient. Moreover, another difficulty in para-Xylene production is similarity in the boiling point of Xylene isomers, which make conventional separations more difficult to separate PX from a mixture of Xylenes [6]. From that perspective, a requirement for overcoming that limitation in Xylene liquid-phase isomerization for a higher-24% yield p-Xylene production is critically considered.

Reactive Distillation has been early attracted as an effective method to carry out processes which are limited by equilibrium limitation. The extensive research, development, and commercialization of reactive distillation were achieved since significant benefits from advanced technology and reduced cost [7, 8]. The effectiveness of using reactive distillation for reactions which have similar behaviors...
with Xylene liquid-phase isomerization such as paraffin isomerization, esterification, etc., is proven by numerous successful processes. Prominent publications and industrial applications of reactive distillation method are shown in Table 1.

Table 1. Examples for industrial applications of reactive distillation.

| Type of reaction | Reaction | Reference |
|------------------|----------|-----------|
| Isomerization    | n-butene ↔ iso-butene | [9] |
|                  | α-isophorone ↔ β-isophorone | [10] |
|                  | cis-2-butene ↔ 1-butene | [11] |
| Oligomerization  | 2 (n-butenes) ↔ octenes | [12] |
| Alkylation       | benzene + ethylene ↔ ethylbenzene | [13] |
| Esterification   | methanol + acetic acid ↔ methyl acetate + water | [14] |
|                  | ethanol + acetic acid ↔ ethyl acetate + water | [15] |
| Etherification   | methanol + isobutene ↔ tert-butyl ether (MTBE) | [16] |
|                  | methanol + isoamylene ↔ tert-amyl ethyl ether (TAME) | [17] |
| Decomposition    | Cumene hydroperoxide ↔ phenol + acetone | [18] |

In this work, the author proposed a basic design and simulation of reactive distillation for para-Xylene production which is aimed to achieve a higher yield of PX by overcoming the equilibrium limitation. An inert solvent will be fed into the reactive distillation to facilitate separation of p-Xylene by extractive function. Xylene catalytic liquid-phase isomerization is carried out and several important design parameters will be varied to study behaviors of the system.

2. Xylene isomerization in liquid phase

The liquid-phase isomerization of Xylenes in free of ethylbenzene can be carried out by acid-functional heterogeneous catalysts. The process involves several intermediate conversions, e.g. protonation, dealkylation and transalkylation [19]. Many types of zeolites have been investigated for Xylene isomerization in liquid phase such as H-ZSM-5 [20], platinum-modified H-ZSM-5 [21], USY-zeolite [2, 22] and Y-zeolite[23]. In this work, a ZSM-5 zeolite will be considered for catalysis of p-Xylene production and kinetic data from published by Cappellazzo et al. (1991) [4] will be used.

2.1 Reaction and thermodynamics

The triangular scheme for Xylene liquid-phase isomerization was proposed by Hopper and Shigemura (1973) [3] and Norman et al. (1976) [24] in publications on using zeolite catalysts for this reaction. As shown in figure 1, Xylenes including ortho-, meta- and para-isomers are noticed by OX, MX, and PX, respectively. The mechanism was further confirmed by an investigation from Olson et al. (1981) [25] into the diffusion coefficient of components during isomerization. Three reversible conversions occur simultaneously with different rate constants (k_i) until the reaction approaches equilibrium state.

![Figure 1. Triangular scheme of Xylene isomerization.](image)

Thermodynamic data of Xylene isomerization was studied by Chirico and Steele (1997) [26] in the liquid phase at 323K of temperature. The dependence of equilibrium constant on temperature was accomplished by Jonathan C. G. and Alírio E. R. (2013) [27] that in the range from 250K to 550K, they computed logarithms of reaction constants as functions of temperature. The composition distribution of Xylene isomerization reported by Jonathan and co-worker [27] illustrated the
equilibrium limitation of this reaction. It is known that the maximum yield of para-isomer at equilibrium state can only be obtained of 24% mol. In agreement with this conclusion, results from a simulation study by Minceva et al. (2007) [5] also depicted thermodynamic limitation in Xylene isomerization.

2.2 Kinetic Data

In this study, kinetic data of Xylene liquid-phase isomerization published by Cappellazzo et al. (1997) [4] will be used. They carried out conversions under the catalysis of ZSM-5 zeolite in range 523K - 573K of temperature and modeled the reaction kinetics according to the triangular scheme in figure 1. With the assumption of a single-site, surface rate controlled model of Langmuir-Hinshelwood kinetics, rates of interconversion reactions are expressed as functions of the corresponding values of rate constants, concentrations of Xylenes, and adsorption equilibrium constants.

The influence of temperature on the model kinetic parameters was taken into account by Arrhenius-type relationships. Values of rate constants and activate energy of forward reactions at the temperature of 553K were accomplished by Cappellazzo et al. The values of backward interconversion would be calculated by relations between the corresponding equilibrium constants and rate constants.

| i | $k_i \times 10^9$ (m²·s⁻¹·kg⁻¹) | $E_i$ (kJ/mol) |
|---|---|---|
| 1 | 0.64 | 98.65 |
| 2 | 1.06 | 135.85 |
| 3 | 0.58 | 158.00 |

3. Design of process

3.1 Conceptual design

In this work, in order to overcome the equilibrium limitation of Xylene isomerization, para-Xylene is conceptualized to be continuously removed out of the reactive environment as the product in the distillate stream (because p-Xylene is the lowest boiling-point component in system). The conversion forward to p-Xylene formation could thus be shifted and the yield of para-isomer would be enhanced over than 24% (equilibrium limitation). The same principle has been successfully applied for numerous researches and industrial applications shown in Table 1.

The insignificant difference in boiling points of Xylenes makes conventional separations of p-Xylene from other isomers difficult [6]. In this study, to facilitate the purification of p-Xylene from the other, an inert solvent (S) with a significantly higher boiling point than Xylenes is chosen as a vapor depressant for extractive distillation inside reactive distillation column. The feasibility of this method has been accomplished by publications on other reactive systems with similar behavior [28, 29].

In final, the structure of a reactive distillation column in this work is schematically proposed by the author as shown in Figure 2. The arrangement is inspired by an exemplary two-feed reactive distillation column for methyl acetate production by Bessling et al. (1990) [30]. The product (methyl acetate) in that process, which is the lowest boiling-point compound and forms the azeotropes with other components, is also extracted by non-reactive extractive stages inside the column by acetic acid and withdrawn overhead in high purity.

From the top of the column, there are three sections functionalized with rectification, reaction and stripping, respectively. In this work, for simplicity to case studies, the rectifying portion is considered as a combination of a conventional rectifier overhead column and an extractive section. An inert solvent (S) will be entered into the rectifying section, near the top of the column to form the vapor of “heavier” Xylenes (ortho- and meta-isomer) flowing up to go down. This results in high purity of para-Xylene in product stream as overhead effluent. Moreover, the presence of solvent stream facilitating extraction of p-Xylene will accelerate isomerization forwards to para-isomer formation. The yield of p-Xylene can be therefore achieved higher than equilibrium limitation (24% mol).
Below the rectifying section, reactive stages with catalyst are set up for Xylene isomerization. In this section, Xylenes in liquid stream are converted between isomers in which p-Xylene is the desired product in this process. After reactions, Xylene isomers in the vapor phase will flow up through the rectifying section where para-Xylene will be extracted and purified before going off in the product effluent overhead. The liquid phase of the mixture after isomerization flows down and passes through the stripping zone.

In the bottom, the stripping zone is designed to deal with separating almost the solvent S and a part of non-reacted o-Xylene and m-Xylene out of reactive distillation column. The end stream withdrawn from this column will be sent to a recovery column to segregate and separately recycle high-quality streams of solvent and non-reacted Xylenes.

3.2 Important designs of process

Flowsheet of the process involves a reactive distillation column and a recovery column as shown in figure 3. In this work, the effects of certain important steady-state design variables of reactive distillation column on process performance are the most considerations to study. The recovery column will be set up so that the quality of its effluents adapts to the composition requirement for recycle. Because the behavior of reactive distillation essentially attributes the performance of process, the evaluation to process is based on the yield of p-Xylene and basic energy factors including ratios of reflux (RR) and boil-up (BR) of reactive distillation column. A similar approach can be found in a publication on design and control reactive distillation by W. L. Luyben and C.-C. Yu (2009) [31].

3.2.1 Design variables. In this work, design variables of reactive distillation column for process include: i) number of reactive stages ($N_{Rxn}$); ii) number of rectifying stages ($N_a$) and iii) number of stripping stages($N_b$). The effect of each chosen variable on the process performance is studied by changing the value of that variable and evaluating the performance of process; while values of the other are remained.

The flowsheet is shown on the flowsheet in figure 3. The Xylene make-up stream is assumed to contain three Xylene isomers with a composition of a raffinate stream from the PAREX unit. Make-up stream of solvent is set up to the purity of S at 100%. The quality of the product stream is fixed to 95.0% molar of para-Xylene in all case studies. The bottom effluent from the reactive distillation column is maintained at 0.1% molar of p-Xylene. This concentration is advantageous for operation stability of the consecutive recovery column. The recycled streams are monitored as shown in Figure 3 to ensure the purity of streams for rectification and reaction and thus, accomplish the efficiency of the process.
3.2.2 Evaluation to process. The process will be evaluated by two factors: i) yield of para-Xylene (PX) and ii) ratios of reflux (RR) and boil-up (BR) of reactive distillation column (RDC). Because the aim of this work is to overcome equilibrium limitation in Xylene isomerization for PX production, the yield of PX firstly needs to be achieved larger than the limitation, 24% molar of Xylenes in conversion to PX. Additionally, the change in values of RR and BR of RDC will behave the nature of the system and provide important implications for further optimization of the process.

$$\text{Yield PX(%) } = \frac{x_{\text{PX}}^pD - x_{\text{PX}}^pF_X}{(x_{\text{OX}}^p + x_{\text{MX}}^p)F_X} \times 100$$

In which,

- $x_B^A$: molar fraction of compound B (OX, MX, PX) in stream A (product P, Xylene F) of the RDC.
- D: distillate rate of the RDC (kg-mole/ h) and F_X: feed Xylenes rate (kg-mole/ h).

4. Simulation of process

The effects of design variables chosen on process performance will be simulated while the values of the other remain as shown in table 3.

| Variable                  | Notation | Fixed value |
|---------------------------|----------|-------------|
| Number of rectifying stages | $N_R$   | 60          |
| Number of reactive stages  | $N_{Rxn}$ | 50          |
| Number of stripping stages | $N_S$   | 10          |

4.1 Effect of number of reactive stages ($N_{Rxn}$) on process

4.1.1 Effect of $N_{Rxn}$ on p-Xylene yield. The effect of reactive stages number on the yield of para-Xylene is shown in Figure 4. Overcoming equilibrium limitation can be accomplished in all values of $N_{Rxn}$ is case-studied. The yield of para-Xylene increases from 25.4% to 29.0% when the number of reactive stages varied from 20 to 100 theoretical trays. In the initial time, the yield has significant
increments along with the increasing reactive tray number until this design variable approach 50 trays, corresponding to 28.55% of p-Xylene yield. After that, p-Xylene can be obtained more slightly if the number of reactive stages is increased and there will be almost no more the desired product formed when the number of reactive stages is larger than 70 trays.

This effect can be explained as the more reactive trays are set up, the more hold up of reactants in liquid streams is accumulated in the reactive distillation column (RDC). This leads to a larger Damkoler number (Da) of RDC and therefore, the Xylene liquid-phase isomerization results in a higher yield of para-isomer. There are more than 50 reactive trays; however, the Da is large enough and the conversions will start to approach the equilibrium design for configuration of this reactive distillation column. So, the yield of para-Xylene is no longer enhanced after there are more than 70 trays set up for the RDC. The similar behavior can be seen in a study by Huss et al. (2003) [32].

![Figure 4](image-url)  
**Figure 4.** Effect of reactive stages number of RDC on p-Xylene yield.

4.1.2 Effect of $N_{Rxn}$ on energy factors. Figure 5 depicts the effects of the reactive stage number of reactive distillation column (RDC) on its reflux ratio (RR) and boil-up (BR) ratio. The values of RR and BR are significantly decreased when the RDC has a higher number of reactive stages. Until there are around 50 trays in the reactive section, the reflux- and boilup-ratios start to approach the minimum values. In this period, the behavior of the reactive distillation column agrees with those of a conventional distillation system. However, values of RR and BR will be slightly increased after more than 75 reactive trays is configured for the RDC. When the number of reactive stages is set up from 75 to 100 trays, then values of RR and BR will be increased from 14.30 to 14.41 and from 1.697 to 1.703, respectively. This behavior of the RDC would be recognized in many similar reactive distillation systems [31].

The explanation is the change in composition profiles in the column when the number of reactive stages is varied. If the reactive portion is set up increasingly for a number of trays from 20 to 100, then the compounds flowing through a thicker stage of catalyst will react or/ and accumulate more and present less than those of that at the opposite ends of the column. The concentration of the “lightest” impurity (m-Xylene) in the rectifying section will be decreased but those of the product (p-Xylene) in the stripping zone will be simultaneously increased. Therefore, a reduced value of RR can be used to keep the quality of overhead stream but a higher value of BR is critical to maintain the specifications of the end effluent of the RDC. Reversibly, the concentration of the “heaviest” component (solvent S) in the rectifying section will be increased but those of that in stripping zone will be simultaneously decreased. Therefore, the $N_{Rxn}$ is increased then the value of RR needs to be larger enough to purify p-Xylene out of “heavier key” in the overhead stream; while a lower BR can be kept to separate the solvent out of p-Xylene at the bottom. The competition of these tendencies in the change of the reflux ratio and boilup ratio of the RDC makes the counterintuitive behavior when the number of reactive trays is varied.
Figure 5. Effects of reactive stages number of RDC on its: a) Reflux ratio; b) Boil-up ratio.

4.2 Effect of number of rectifying stages (\(N_R\))

4.2.1 Effect of \(N_R\) on para-Xylene yield.

The effect of reactive stages number on the yield of para-Xylene is shown in figure 6. The equilibrium limitation can be overcome in all case studies about values of \(N_R\). The yield of para-Xylene increases from 26.7% to 29.2% when the rectifying number is set up from 40 to 100 trays. The increment of PX yield is large in the beginning until there are 60 trays in the rectifying section. If more than that number of trays configured in this zone, the yield of the desired product can be more slightly obtained.

Figure 6. Effect of rectifying stage number of RDC on para-Xylene yield.

The explanation for this behavior is that the more rectifying trays are used, the more effective separation of para-Xylene is achieved. Because the product quality in the overhead stream is fixed (95% molar PX), effective separation leads to a higher yield of more p-Xylene. Additionally, isomerization and separation simultaneously occur inside the reactive distillation column; thus a better rectification will result in forward shifting conversions to the formation of para-Xylene. The yield of PX only slightly increase when there are more than 60 rectifying trays. This implies the reactive distillation column with that configuration approaches equilibrium design.
4.2.2 Effect of $N_R$ on energy factors. Figure 7 depicts the effects of the reactive stage number of reactive distillation column (RDC) on its reflux ratio (RR) and boil-up (BR) ratio. In the beginning, the values of RR and BR are significantly decreased when the RDC has more trays for rectification. However, the reflux- and boilup-ratios are insignificantly reduced or not changed once the number of rectifying trays is increased to be higher than values of 60. This behavior of the reactive distillation column agrees with those of a conventional distillation system.

![Figure 7](image-url)

**Figure 7.** Effects of rectifying stage number of RDC on its: a) Reflux ratio; b) Boil-up ratio.

4.3 Effect of number of stripping stages ($N_S$)

4.3.1 Effect of $N_S$ on p-Xylene yield.

The effect of reactive stages number on the yield of para-Xylene is shown in Figure 8. The equilibrium limitation can be overcome if the value of $N_S$ is lower than 13 trays. The yield of para-Xylene will be strongly decreased in linearity from 37.28% to 1.69% when the number of stripping stages is varied from 6 to 30 trays. This behavior can be explained that setting up more trays in the stripping section while fixing the feed location of the solvent stream will make portions of rectification and stripping relatively closer; so the efficiency of para-Xylene separation in rectifying section is reduced and thus the yield of PX is decreased.

![Figure 8](image-url)

**Figure 8.** Effect of stripping stage number of RDC on p-Xylene yield.
4.3.2 Effect of $N_s$ on energy factors. Figure 9 depicts the effects of stripping stage number of reactive distillation column (RDC) on its reflux ratio (RR) and boil-up (BR) ratio. When the number of stages in the stripping zone starts to increase, the values of RR and BR strongly decrease. However, the reflux ratio will be insignificantly reduced once more than 15 trays set up in the stripping section. Similarly, the boil-up ratio is also decreased when the stripping stage number is increasingly varied. The number of stripping stages begins to slightly affect the value of BR when the zone for stripping has more 20 trays. This behavior is in agreement with those of a conventional distillation system.

![Figure 9](image_url)

**Figure 9.** Effects of stripping stage number of RDC on its: a) Reflux ratio; b) Boil-up ratio.

5. Conclusion

In this work, the author proposed a basic design and simulation of reactive distillation for para-Xylene production. An inert solvent was introduced into the reactive distillation column to facilitate the separation of p-Xylene and shift the conversions forward the formation of PX. Several important design parameters would be varied to study the behaviors of the system. Evaluation of process performance was chosen as the para-Xylene yield and energy factors (reflux- and boil-up ratios).

The equilibrium limitation of Xylene liquid-phase isomerization (24%molar of PX) could be overcome by using configurations of the reactive distillation column proposed in this study. The maximum yield of PX up to 37% molar was obtained in a reactive distillation column configuration in which tray number of reactive-, rectifying- and stripping section is of 60, 50 and 6, respectively.

The change of energy factors (reflux- and boil-up ratios) was observed at different behaviors corresponding to the variation of rectifying-, reactive- and stripping stage number. Counterintuitive behavior of energy factors, when the number of reactive stages was changed, is the existence of minimum values of reflux-and boil-up ratios. Reversibly, those energy factors of the reactive distillation column showed a common behavior of a conventional distillation system in all case studies of change in rectifying-and stripping stage number.

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