

# Xylene Transformation over USY Zeolite: An Experimental and Kinetic Study

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## Abstract

A systematic study on the influence of reaction conditions (temperature, time, and reactant type) on the selectivity of xylene transformation has been carried out over USY zeolite. Initial product selectivity revealed that both isomerization and disproportionation of xylenes are primary reactions. Higher conversion was observed with p-xylene reactant as compared to m- and o-xylene. The “reactant converted” deactivation model was tested with xylenes as model compounds, using effective, mechanistic kinetic models, developed from the transformation of each xylene isomers. The parameters optimized to the experimental data gave a good prediction of the overall reaction kinetics for the xylene transformations. The results provide significant evidence that the “reactant converted” decay model can be adequately utilized to account for catalyst deactivation of the xylene transformation.

Keywords: Xylene transformation, catalyst deactivation model, kinetic modeling, USY zeolite, fluidized-bed reactor.

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## 1. Introduction

The demand for xylenes as a raw material for polyester fibers and films continues to grow, and drive the search for improved xylene isomerization processes. Most of the currently working isomerization plants are using zeolites based catalysts. It is well-known that xylenes undergo two main competitive reactions, isomerization and disproportionation over zeolite catalysts. However, it is usually desired to minimize disproportionation in favor of isomerization reaction, especially to para-isomer. Thus, three types of selectivity can be defined, isomerization, disproportionation, and distribution of trimethylbenzene isomers (TMBs) [1]. The isomerization selectivity has been shown to depend mainly on the diffusion path of xylenes, while that of trimethylbenzenes distribution and disproportionation selectivity both depend on the diffusion path, size, and shape of cavities or channel intersections [2]. Moreover, the p-xylene/o-xylene (P/O) ratio during xylene transformation has also been utilized as a tool to characterize zeolite pore structure [2-7].

Surveying the present literature on the isomerization of xylenes, it appears that systematic studies which focus on the influence of reaction parameters (reaction time, temperature, and conversion) on the three types of selectivity mentioned above are scarce. Thus, with this in mind we explore the possibility of a systematic study on the influence of reaction parameters on the isomerization and disproportionation selectivity during the transformation of the three xylene isomers.

Regarding the kinetics of xylene transformations over zeolitic catalysts, several modeling techniques have been applied to obtain the numerous kinetic parameters of this

complex reaction system. Amongst the techniques employed in the literature include: analytical methods such as Wei-Prater method [8,9,10], Laplace transform [11], and finite integral transform [12, 13]. Curve fitting method, such as Himmelblau method [14, 15], and least-squares method [16, 17] have also been applied. Recently, Iliyas and Al-Khattaf [18] proposed a new modeling procedure based on the isomerization of the each xylene isomers. The various kinetic parameters of the overall m-xylene transformation were obtained from simplified effective kinetic models.

However, in most of the previous kinetic studies on xylene transformation, the deactivation of the catalyst was not adequately accounted for, in the development of kinetic models used in such studies. Moreover, the limited papers, which incorporated a catalyst deactivation function, used the time on stream (TOS) decay model [14, 18, 19, and 20]. This deactivation function is empirically based, as it does not incorporate a mechanistic description of catalyst deactivation [21]. On the other hand, since coke deposition is the major cause of catalyst deactivation in the transformation of xylenes, the “reactant converted” decay model, proposed by Al-Khattaf and de Lasa [22] will be employed in this work. This important deactivation model has been successfully tested for modeling of 1,2,4 trimethylbenzene reactions [21], cracking of cumene [22, 23], and 1,3,5-triisopropylbenzene [24].

The second part of the present study is aimed at modeling the kinetics of xylene transformation over a USY zeolite by using the “reactant converted” catalyst deactivation model. The modeling procedure proposed in our previous work [18], will be employed to obtain the kinetic constants for the reaction. The xylene transformation will be carried out

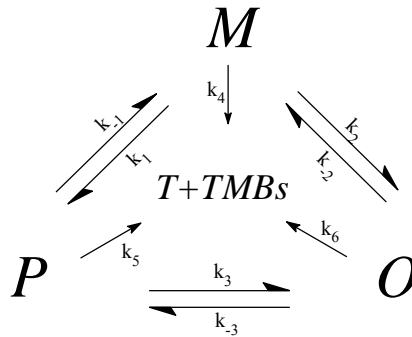
using the riser simulator. This reactor has been shown to overcome the limitation of temperature/concentration gradients associated with fixed-bed and other reactor types. Besides, utilizing the riser simulator is more relevant in testing the new catalyst deactivation model, because it ensures uniform coke deposition on the catalyst particle due to the intensified fluidization, and well-mixed characteristics of this reactor. Also, performing xylene transformation using the riser simulator is practically relevant. This is because it can adequately mimic the transformation of the C<sub>8</sub> aromatic compounds (including the three xylene isomers) in the catalytic cracking unit of the refinery, which is similar to riser simulator used in the present study.

## 2. Experimental Section

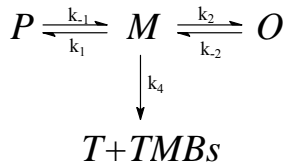
Ultrastable Y zeolite (USY) used in this study was obtained from Tosoh Company. The Na zeolite was ion exchanged with NH<sub>4</sub>NO<sub>3</sub> to replace the sodium cation with NH<sub>4</sub><sup>+</sup>. Following this, NH<sub>3</sub> was removed and the H form of the zeolite was spray-dried using kaolin as the filler and silica sol as the binder. The resulting 60- $\mu$ m catalyst particles had the following composition: 30 wt % zeolite, 50 wt % kaolin, and 20 wt % silica sol. The process of sodium removal was repeated for the pelletized catalyst. Following this, the catalyst was calcined for 2 h at 600 °C. Finally, the fluidizable catalyst particles (60  $\mu$ m average size) were treated with 100 % steam at 760 °C for 5 h. The unit cell size (24.28 Å) was determined by X-ray diffraction following ASTM D-3942-80. Surface area (155 m<sup>2</sup>/g) was measured using the BET method with crystal size of 0.9  $\mu$ m. A detailed description of riser simulator [25], experimental procedure, and product analysis has been given in our previous paper [18].

### 3. Kinetic Model Development

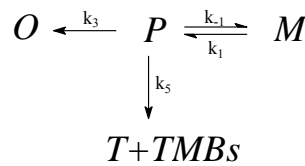
To develop a suitable kinetic model representing the overall transformation of m-xylene, we propose the reaction network shown in Scheme 1. However, the reaction schemes 2-4, which are based on the transformation of each of the each xylene isomers, will be employed to obtain the numerous kinetic parameters of Scheme 1. The details of this analysis can be found in Ref. 18



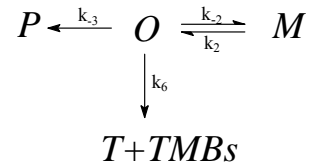
Scheme 1



Scheme 2



Scheme 3



Scheme 4

The riser simulator mass balances based on the schemes 2-4 can be expressed as follows:

m-xylene (Scheme 2):

$$\frac{dy_m}{dt} = -[(k_1 + k_2 + k_4)y_m - \frac{k_1}{K_{pm}}y_p - \frac{k_2}{K_{om}}y_o] \frac{W_c}{V} \exp[-\lambda_m(1 - y_m)] \quad (1)$$

$$\frac{dy_p}{dt} = [k_1 y_m - \frac{k_1}{K_{pm}} y_p] \frac{W_c}{V} \exp[-\lambda_m (1 - y_m)] \quad (2)$$

$$\frac{dy_o}{dt} = [k_2 y_m - \frac{k_2}{K_{om}} y_o] \frac{W_c}{V} \exp[-\lambda_m (1 - y_m)] \quad (3)$$

$$\frac{dy_d}{dt} = k_4 y_m \frac{W_c}{V} \exp[-\lambda_m (1 - y_m)] \quad (4)$$

Following the same procedure, the mathematical models for the simplified kinetic schemes (Schemes 3 and 4) and the overall reaction (Scheme 1) can be developed. The concentration of any species  $i$  in the above equations is related to its mass fraction as follows:

$$C_i = \frac{y_i W_{hc}}{MW_i V} \quad (5)$$

while the influence of temperature on the model parameters can be accounted for, through the following Arrhenius equation:

$$k_i = k_{0i} \exp\left(\frac{-E_i}{R} \left[\frac{1}{T} - \frac{1}{T_0}\right]\right) \quad (6)$$

$T_0$  is the average reaction temperature introduced for reparametrization of kinetic constants [26]. As mentioned earlier, the “reactant converted” decay function ( $\varphi = \exp[-\lambda_i(1 - y_i)]$ ) is employed in the mathematical models to account for catalyst deactivation.

In order to ensure thermodynamic consistency at equilibrium, the rate constants for  $m$ - to  $p$ -xylene, and  $m$ - to  $o$ -xylene reactions in the above equations are expressed as follows [13]:

$$k_{-1} = k_1/K_{pm} \quad (7)$$

$$k_{-2} = k_2/K_{om} \quad (8)$$

where  $K_{pm} = (C_p/C_m)_{eq}$  and  $K_{mo} = (C_o/C_m)_{eq}$  are temperature-dependent equilibrium constants for both reactions, respectively. However, an average value can be computed for both constants, because the thermodynamic equilibrium concentrations of the xylenes remain fairly constant within the temperature range of this work. The xylene equilibrium concentrations are obtained from a published work [27].

Each set of equation for the simplified models involves seven adjustable model parameters that have to be estimated before a solution is obtained. These parameters were adjusted using the weighted least-square algorithm for nonlinear parameters in a MATLAB package. The results obtained in this regard are presented and discussed in subsequent sections.

## 4. Results

### 4.1 *m*-Xylene transformation

The transformation of *m*-xylene over the USY zeolite produces *p*-xylene, *o*-xylene, toluene, and trimethylbenzenes. The isomerization and disproportionation selectivity obtained during *m*-xylene reaction is shown in Fig. 1. It can be observed from this figure that isomerization and disproportionation selectivity are almost identical. Furthermore, the P/O ratio (Fig. 2) is consistent with the thermodynamic predicted value of 1.09.

It has been mentioned earlier that disproportionation reaction is a major reaction pathway during the transformation of xylenes over large pore zeolites such as USY zeolite used in this study. As a result, the distribution of trimethylbenzenes can give further

insight into the initial products of disproportionation reaction. Thus, Fig. 3 presents the distribution of TMBs isomers obtained with m-xylene disproportionation. Indeed, it is obvious that 1,2,4- and 1,3,5-TMBs are primary products of m-xylene disproportionation, while 1,2,3-TMB is not. Furthermore, the plot of toluene to trimethylbenzenes (T/TMBs) mole ratio presented in Fig. 4 depicts a high initial value, which decreases exponentially as conversion increases. Beyond 5% conversion, the ratio can be observed to remain constant at a value 20-30 % above the stoichiometric ratio of 1.0.

#### **4.2 *p*-Xylene transformation**

The conversion of p-xylene produces m-xylene, o-xylene, toluene, and trimethylbenzenes. The initial selectivity to isomerization and disproportionation during the reaction of p-xylene appears to be similar (Fig. 5). Whatever the reaction condition, the ratio of m-xylene/o-xylene (M/O) obtained with p-xylene transformation is much higher than the thermodynamic value of 2.0. Also, the plot of M/O ratio as a function of p-xylene conversion at different reaction temperature (Fig. 6) shows that it varies more with reaction temperature than conversion.

With p-xylene transformation, 1,3,5- trimethylbenzene approaches zero at low conversion, while 1,2,3 and 1,2,4 isomers did not appear to extrapolates to zero under similar conversion level (Fig.7). Moreover, the ratios of the three trimethylbenzene isomers produced approaches equilibrium value after 15% p-xylene conversion is attained. This result agrees with the work of Collins et al. [10]. The plot of toluene to trimethylbenzene (T/TMB) mole ratio versus p-xylene conversion gives a similar trend to



that obtained with respect to m-xylene (Fig. 8), although, the ratio can be observed to be constant at a slightly higher value than with m-xylene.

### ***4.3 o-Xylene transformation***

Unlike m- and p-xylene, o-xylene did not react to any appreciable extent at 350°C. The trend of initial selectivity to isomerization and disproportionation (Fig. 9), m-xylene/p-xylene (M/P) ratio (Fig. 10), trimethylbenzenes distributions (Fig.11), and T/TMB mole ratio (Fig.12) as a function of o-xylene conversion were very similar to those obtained with p-xylene (refer to the preceding section). M/P ratio appears to be unaffected by increasing conversion level, whereas it decreases steadily with increasing reaction temperature.

### ***4.4 Comparison between the transformation of the xylene isomers***

Data presented in Fig. 13 indicate that the reactivity of the xylene isomers decreases in the following order: p-xylene > m-xylene > o-xylene. Moreover, it can be observed that the xylene isomers undergo disproportionation to different extent, with higher disproportionation accompanying p-xylene than either m- or o-xylene transformations as shown in Fig. 14.

## **5. Discussion**

### ***5.1 m-Xylene transformation***

The plot of initial selectivity to isomerization and disproportionation during m-xylene transformation shown in Fig. 1 indicates that both the isomerization and disproportionation are primary reactions. Moreover, as the level of m-xylene conversion

increases disproportionation becomes more pronounced since the produced xylenes also contributes to the overall disproportionation reactions.

It is remarkable that the slight increase in the disproportionation selectivity with increasing conversion level (Fig. 1) differs from some previously reported trend [28-30]. Indeed, it is well-known that xylene disproportionation is a bimolecular reaction, which requires a higher concentration of acid sites. When these sites are selectively covered by coke precursors, it loses its activity. This results in the decrease of disproportionation selectivity with increasing time on stream [29]. The trend observed in the present study could be explained due to the following; the contact time for xylene transformation in this study is much smaller (<15 s) than most of the previous studies. This reduces the deactivation of the strong active sites of USY zeolite, since trimethylbenzenes which are necessary intermediates for the formation of coke precursors cannot undergo secondary transformation. Besides, the low acid concentration (0.033 mmol/g) of the USY used in the present study contributes to this observation. In addition, the negligible coke deposition (< 0.1 wt %) measured for different the reaction condition over the USY catalyst [31] further substantiates the foregoing explanation. Thus, it could be said that this study focuses on the initial behavior of xylene transformation.

It is interesting to observe that the transformation of m-xylene produced almost equilibrium values of P/O ratio (Fig 2). This can be easily understood since the isomerization of m-xylene to produce p-and o-xylene involves 1, 2 methyl shifts which are identical reactions. Moreover, the cage opening of Y zeolite is large enough, and thus allows the produced isomers to exit the zeolite presumably without any shape selectivity.

Fig. 3 shows that with m-xylene as reactant, 1,2,4- and 1,3,5- TMB isomers are obtained as initial products, however, 1,2,3-TMB appeared as secondary product. It could be that 1,2,3- isomer is formed by secondary isomerization of 1,2,4- and 1,3,5- TMBs under the conditions of this study. In contrast, all the three isomers have been reported as primary products of m-xylene disproportionation in some previous studies [10, 32], however, over metal cation exchanged Y zeolite.

## 5.2 *p*-Xylene transformation

Similar to m-xylene, the transformation of p-xylene proceeds with both isomerization and disproportionation as primary reactions (Fig. 5). This is obvious from the initial selectivity for both reactions. In addition, 1,2,4 trimethylbenzene isomer can be observed to approach zero at low conversions, indicating that it is a primary product for p-xylene disproportionation (Fig. 7). This result is in conformity with some previously published works [10, 32].

The higher M/O ratio beyond the equilibrium ratio of 2.0 (Fig. 6) particularly at lower reaction temperature is most probably due to the difficulty in causing direct conversion of p- to o-xylene. Moreover, the decrease in this ratio from 4.5 to around 3.1 with reaction temperature could be explained due to the ease in causing this reaction with increasing reaction temperature, as will be shown later. Indeed, it has been found that the apparent direct interconversion between p- and o-xylene requires a higher activation energy as compared to 1,2 methyl shift [14, 18, 19]. Thus, a higher reaction temperature is needed to overcome this high energy barrier.

### **5.3 *o*-Xylene transformation**

The plot of initial selectivity to isomerization and disproportionation depicted in Fig. 9, with *o*-xylene transformation is identical to that of *p*-xylene. As in the case of *m*- and *p*-xylenes, this plot clearly shows that both isomerization and disproportionation are primary products of *o*-xylene transformation. Moreover, employing *o*-xylene as reactant 1,2,4- and 1,3,5- are predicted from the directing effect of methyl groups during electrophilic substitution [10]. However, Fig. 11 shows that only 1,2,4- trimethylbenzenes was obtained as initial product during *o*-xylene disproportionation. This behavior can not be associated with shape selective diffusion of the products, because USY zeolite has large pores that can accommodate the bulky trimethylbenzenes isomers. Thus, it is possible that both 1,3,5 and 1,2,3- TMBs are formed from secondary isomerization of the produced 1,2,4- isomer. Collins et al. [10] observed 1,2,4- and 1,2,3- TMBs as primary products, while Lanewala and Bolton [32] reported that only 1,2,4- and 1,3,5 are primary products of *o*-xylene disproportionation.

### **5.4 *Comparison between the transformation of the xylene isomers***

The observed trend in the reactivity of the xylene isomers (Fig. 13) is consistent with some previous studies [1, 32]. This trend could be related to ease of protonation of carbon positions on the aromatic ring for each xylene isomers [5]. With *o*-xylene reactant, the close proximity of both methyl groups results in a pronounced steric hindrance leading to the difficulty of a proton accessing the C<sub>2</sub> atom during intramolecular isomerization reaction. Consequently, *o*-xylene is the least reactive of the three isomers. On the other hand, *m*-xylene with a framework carbon between the two methyl groups has less effect of

steric hindrance, while with p-xylene, the preferred protonation of the most accessible C<sub>4</sub> atom makes it most reactive. Similarly, as shown by Lanewala and Bolton [32], a direct correlation exists between the extent of disproportionation and the conversion of the xylene isomers. Therefore, the higher reactivity of p-xylene may be responsible for its corresponding higher disproportionation rate [18]. This result also agrees with the work of Morin et al. [1] for xylene isomerization over HY zeolite.

The high initial value of T/TMBs mole ratio observed with the transformation of all the three isomers (Fig. 4, 8, and 12) could be due to the slower desorption rate of the bulky trimethylbenzenes isomers as compared to toluene under short reaction time (< 3s). However, as the reaction time increases, T/TMBs mole ratio decreases to around 1.2. The higher initial value of this ratio may be due to the increase on the desorption rate of TMBs from the pore of the USY zeolite. A similar observation regarding the slower desorption rate of TMBs as compared to toluene was also reported in previous studies [2, 33, 34]. In addition, the higher value of T/TMBs above stoichiometric ratio is probably the result of conversion of TMBs to coke molecules.

The approach of the xylene isomers to their equilibrium values (ATE) is defined as [15]:

$$\frac{F_i - P_i}{F_i - E_i} \times 100 \quad (9)$$

where F<sub>i</sub> = feed concentration of species *i*, P<sub>i</sub> = product concentration of species *i*, and E<sub>i</sub> = equilibrium concentration of species *i*. Figures 16-18 present the ATE of the other two xylene isomers as a function of ATE of each xylene reactant. From this plot, it can be seen that p- and o-xylene approaches their equilibrium value at almost the same rate during m-

xylene transformation. This suggests that the transformation of m-xylene to produce p- and o-xylene advance at identical rate, as shown by the estimated kinetic constants below. On the other hand, with the transformation of o-xylene, m-xylene approaches its equilibrium value 1.3 times faster than p-xylene, and with about 70% higher value of ATE. Similarly, m-xylene approaches equilibrium 1.1 times faster than o-xylene and with 50% higher value of ATE during p-xylene transformation. These findings, which agree qualitatively with a previous study [10] suggests that the transformation of xylenes over the USY zeolite used in this study advance in the thermodynamic controlled regime, unlike over ZSM-5 zeolite, where it proceeds in the diffusion controlled regime [9].

### ***5.5 Modeling Result***

The results presented in Table 1 substantiate earlier observation regarding the identical rate of producing p- and o-xylene during m-xylene isomerization. The values of the estimated preexponential factors for both reactions are essentially the same (0.17 m<sup>3</sup>/kg of catalyst s), and also their activation energies are closely similar at 13.7 and 14.1 (kcal/mol), respectively. A similar result was obtained with the time on stream deactivation model [18]. This was explained by the similarity of the two reactions, because both involve the migration of adjacent methyl groups along the aromatic ring. Moreover, the constraint of transition state complexes in conversion of m- to p-xylene, and m- to o-xylene is negligible under the present conditions.

It is of great interest to note that  $E_3$  and  $E_{.3}$  have the highest values (16.7 and 18.1 kcal/mol, respectively). This clearly suggests that the mutual interconversion between p- and o-xylene, is highly temperature dependent, unlike 1,2- methyl shift with lower values

of activation energy ( $\sim 14$  kcal/mol). This significant result is in perfect agreement with some previous studies [14, 18, 19]. Consequently, it could be proposed that under low reaction temperatures ( $< 450^\circ\text{C}$ ), the interconversion of both isomers proceed via m-xylene as an intermediate reaction step (Fig. 15). However, as the reaction temperature is increased beyond  $450^\circ\text{C}$ , both isomers may attain the required energy to interconvert as shown schematically by the dashed-line in Fig 15B and 15C.

In spite of the forgoing discussion on the difficulty of direct interconversion of p- and o-xylene, it could be seen in Table 1 that the conversion of p- to o-xylene has a lower activation energy ( $E_3$ ) and higher preexponential factor ( $k_{03}$ ) than that of o-xylene ( $E_{.3}$  and  $k_{0.3}$ ). This result, which also agrees with the ATE plots (Fig. 16), could be understood, giving that p-xylene reacts to a greater extent than o-xylene over the catalyst used in this study. Also, the kinetic parameters estimated with p-xylene transformation ( $k_{05}$  and  $E_5$ ) indicate a higher disproportionation with this isomer, as compared with m- and o-xylene disproportionation in agreement with data presented in Fig. 14.

### ***5.6. Comparison between experimental results and model predictions***

The overall parity between experimental data and model values for the transformations of m-, p-, and o-xylene gives a correction coefficient of 0.99, 0.98, and 0.99, respectively. Moreover, from the values of the estimated kinetic constants and their corresponding 95% confidence limits (Table 2), it can be argued that these parameters are accurately estimated. Although, the model tended to slightly overpredict the yield of p-xylene from o-xylene transformation and vice versa. This is not surprising, because the direct interconversion of both isomers occurs only at high reaction temperatures,

meanwhile, the model assumes that their direct interconversion proceed right from the onset. The separation of the two modes of conversion for both isomers i.e. via m-xylene as intermediate reaction step, and apparent direct interconversion with different temperature regime, is quite difficult in the same kinetic model.

To check the validity of the estimated kinetic parameters using with the overall kinetic model (Scheme 1), the fitted parameters were substituted into the model developed for this scheme, and the equations were solved numerically using the fourth order Runge-Kutta method. The simulated results were compared with the experimental data as shown in Figure 17. It can be observed from this figure that the simulated results compares fairly well with the experimental data. This provides significant evidence that the overall model could be used for the interpretation of the data obtained during m-xylene transformation in the riser simulator.

In summary, the good agreement between the model and experimental results proves that the “reactant converted” decay model can be used to successfully model the overall xylene transformation. This model correctly captures the deactivation of the catalyst as a function of the reactant concentration. Moreover, it is consistent with the well-established fact that the deactivation of USY zeolite during xylene transformation is caused by the deposition of coke on active catalyst sites.

## **6. Conclusion**

Experimental studies were conducted in a riser simulator to study the influence of reaction parameters on xylene transformation. The selectivity to isomerization, disproportionation, and distribution of trimethylbenzene isomers were also investigated.



Initial selectivity revealed that both isomerization and disproportionation reactions advance as primary reactions. A higher initial value of T/TMBs mole ratio was observed with the three xylene reactants, and this was explained by the slower desorption rate of bulky TMBs isomers under the short reaction time of the riser simulator. p-Xylene was found to be more reactive than the others xylene isomers. This was explained by the higher accessibility of proton to C<sub>4</sub> atom, due to its least effect of steric hindrance.

A recently proposed catalyst deactivation model, so-called “reactant converted” decay model was tested with the transformation of xylenes. Effective, mechanistic kinetic models were developed to describe the transformation of each of the xylene isomers based on the obtained experimental results. The model parameters were estimated using non-linear regression analysis. The parameters optimized to the experimental data gave a good prediction of the overall reaction kinetics for the xylene transformations. Thus, providing significant evidence that the “reactant converted” decay model can be adequately utilized to account for the catalyst deactivation. Moreover, based on the values of the estimated activation energy, it was found that the interconversion of p- and o-xylene is highly temperature dependent, unlike 1,2- methyl shift, which is only slightly dependent on temperature.

## **Acknowledgment**

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## **Nomenclature**

$C_i$  concentration of species  $i$ , (kmole/m<sup>3</sup>)

$CFL$	confidence limit
$C_d$	concentration of disproportionation products ( $T + TMBs$ ) (kmole/m <sup>3</sup> )
$E_i$	apparent activation energy for the $i^{\text{th}}$ reaction (kJ/mole)
$K_{om}$	thermodynamic equilibrium constant for the conversion of $m$ - to $o$ -xylene
$k_i$	apparent rate constant for the $i^{\text{th}}$ reaction (m <sup>3</sup> / kg of catalyst·s)
$k_{oi}$	pre-exponential factor for the $i^{\text{th}}$ reaction (m <sup>3</sup> / kg of catalyst·s)
$K_{pm}$	thermodynamic equilibrium constant for the conversion of $m$ - to $p$ -xylene
$MW_i$	molecular weight of species $i$ (kg/kmole)
$r$	correlation coefficient
$R$	universal gas constant (kJ/kmole K)
$s$	seconds
$t$	reaction time (s)
$T$	toluene
$T_o$	average temperature of the experiment
$TMBs$	trimethylbenzenes
$V$	riser simulator volume
$W_c$	catalyst mass (kg of catalyst)
$W_{hc}$	mass of hydrocarbon injected into the riser simulator
$y_d$	mass fraction of disproportionation products
$\varphi$	apparent deactivation function
$\lambda$	catalyst deactivation constant

Subscripts

<i>m</i>	meta-xylene
<i>o</i>	ortho-xylene
<i>p</i>	para-xylene
<i>eq</i>	equilibrium

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Table 1. Estimated kinetic parameters

	$E_1$	$E_2$	$E_3$	$E_{-3}$	$E_4$	$E_5$	$E_6$
	13.7	14.1	16.7	18.1	18.7	10.3	13
95% CL	1.9	1.8	7.2	7.9	1.4	1.14	0.15
	$k_{01} \times 10^3$	$k_{02} \times 10^3$	$k_{03} \times 10^3$	$k_{-03} \times 10^3$	$k_{04} \times 10^3$	$k_{05} \times 10^3$	$k_{06} \times 10^3$
	0.17	0.17	0.059	0.038	0.38	0.41	0.25
95% CL	0.02	0.02	0.027	0.019	0.035	0.03	0.02
	$\lambda_m$	$\lambda_p$	$\lambda_o$				
	0.83	1.8	1.5				
95% CL	0.12	0.9	0.9				

$k_i$  ( $m^3/ kg \text{ of catalyst} \cdot s$ )

$E_i$  (kJ/mole)

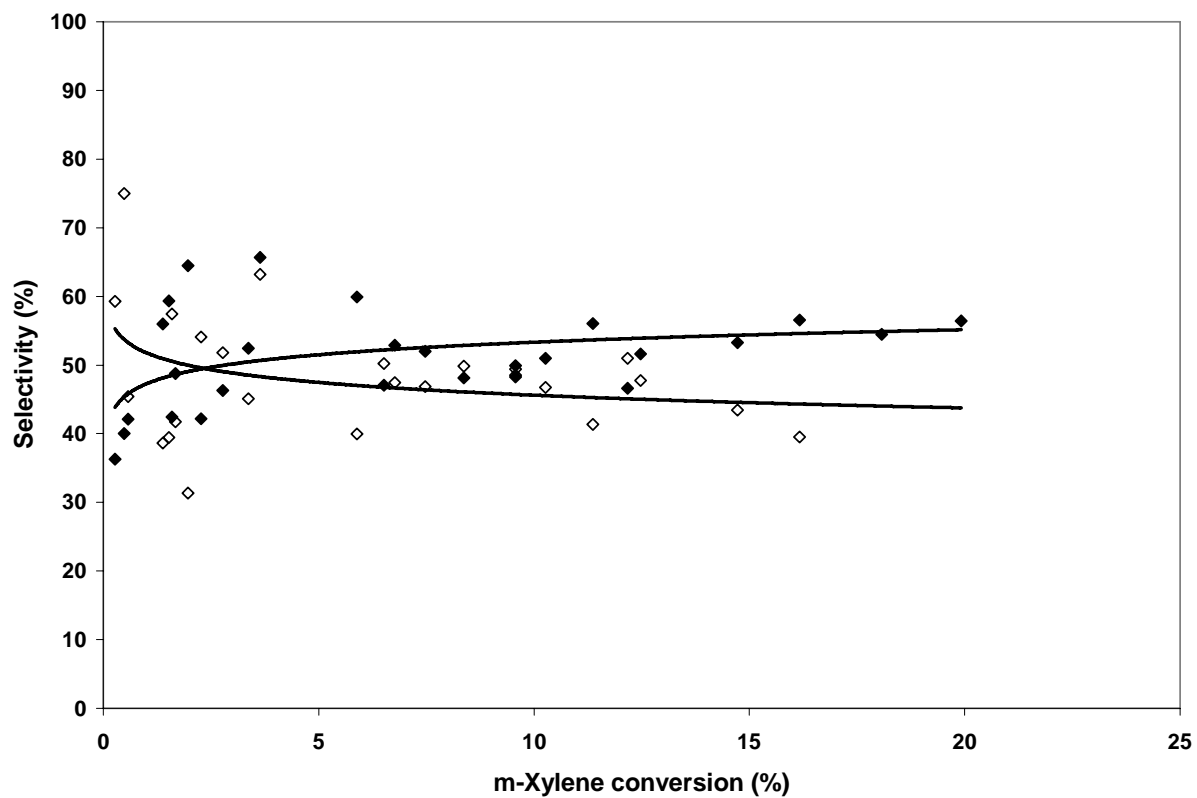


Fig.1. Isomerization and disproportionation selectivity during the transformation of m-xylene as a function of conversion. (◇) isomerization; (◆) disproportionation.

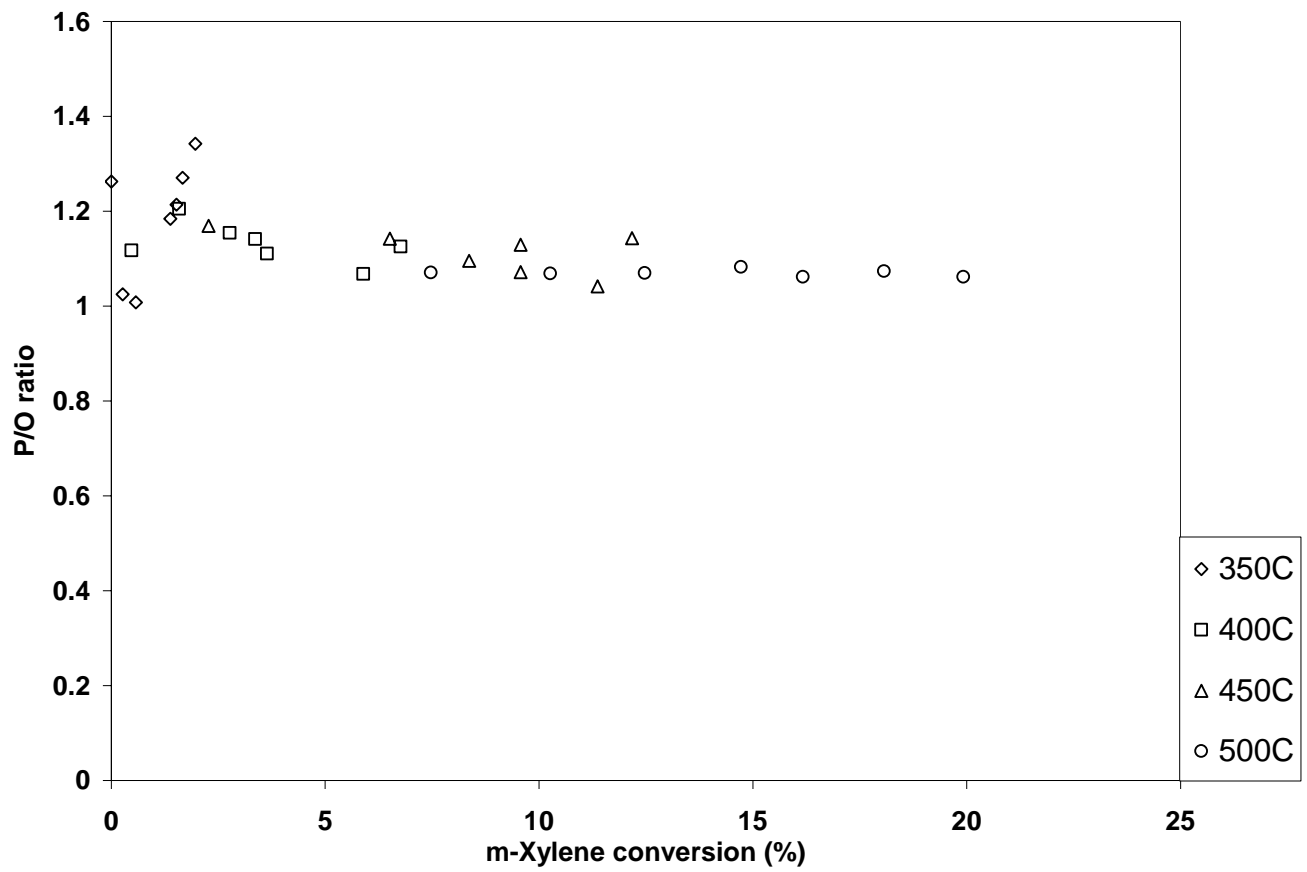


Fig.2. p-xylene/o-xylene (P/O) ratios vs. m-xylene conversion at different temperatures

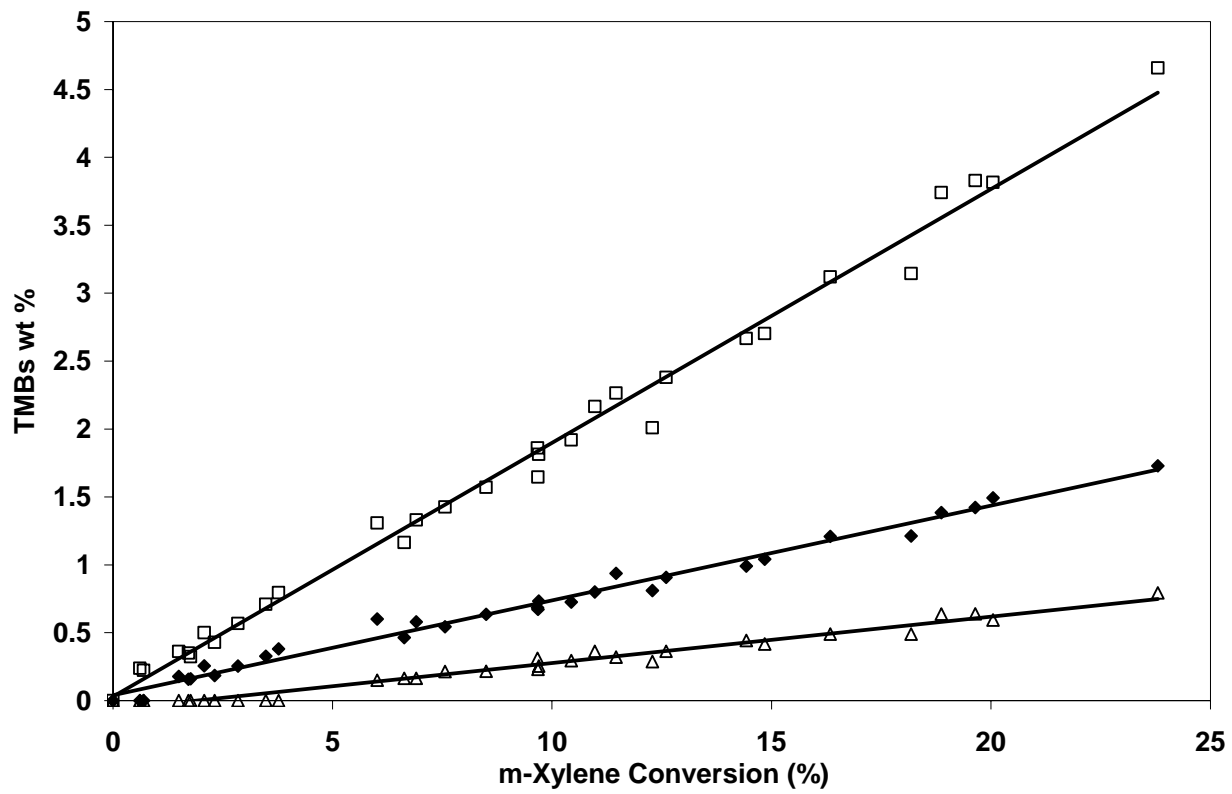


Fig.3. Distributions of trimethylbenzenes isomers as function of m-xylene conversion  
 (Δ) 1,2,3-TMB, (□)1,2,4-TMB, (◆) 1,3,5- TMB



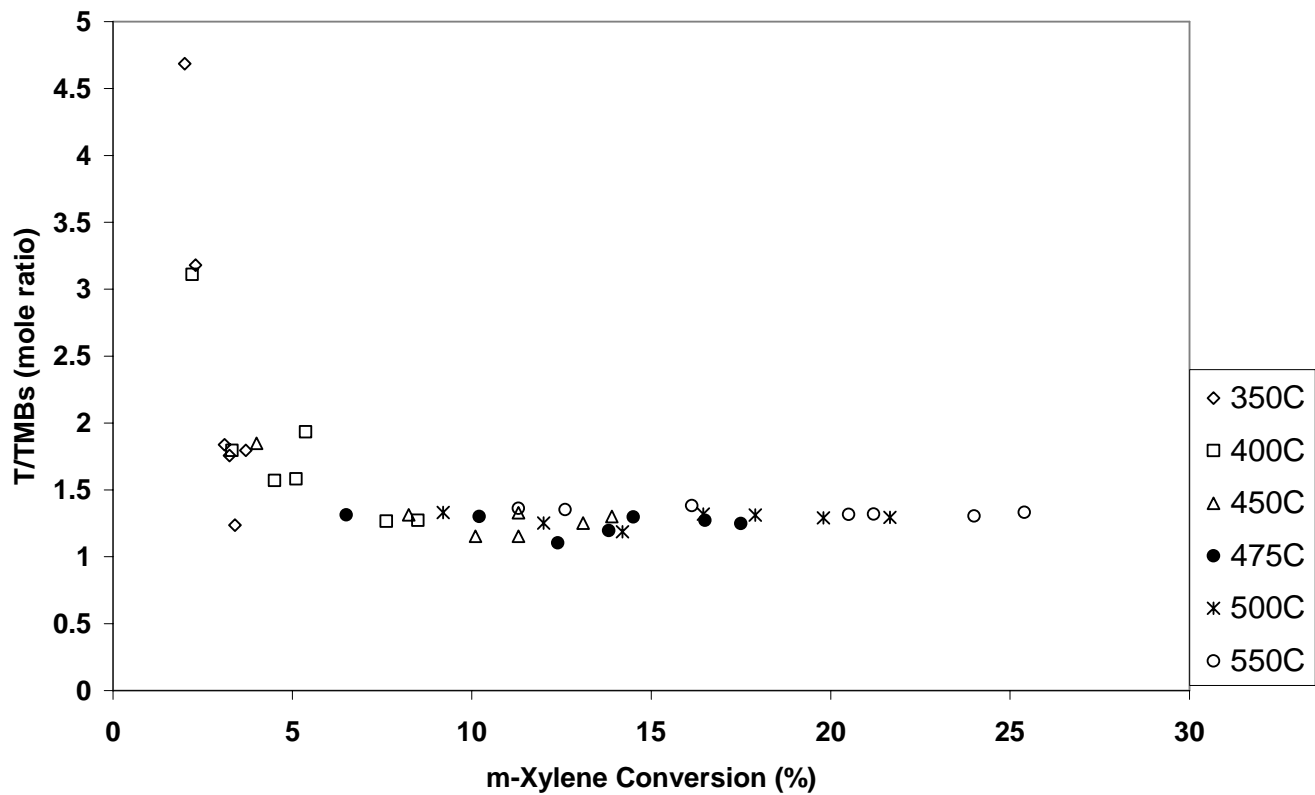


Fig. 4. Molar ratio of toluene to trimethylbenzene as a function of m-xylene conversion at different reaction temperatures

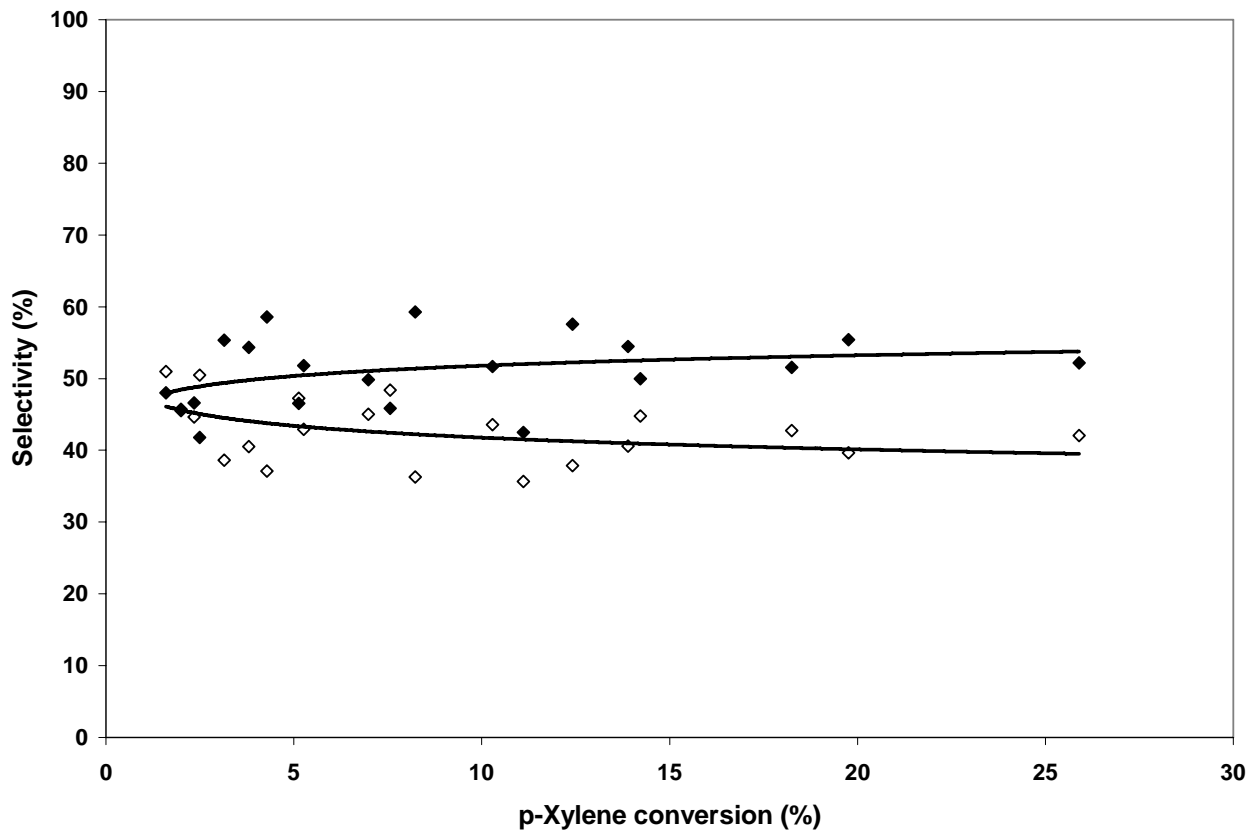


Fig.5. Isomerization and disproportionation selectivity during the transformation of p-xylene as function of conversion. (◇) isomerization, (◆) disproportionation

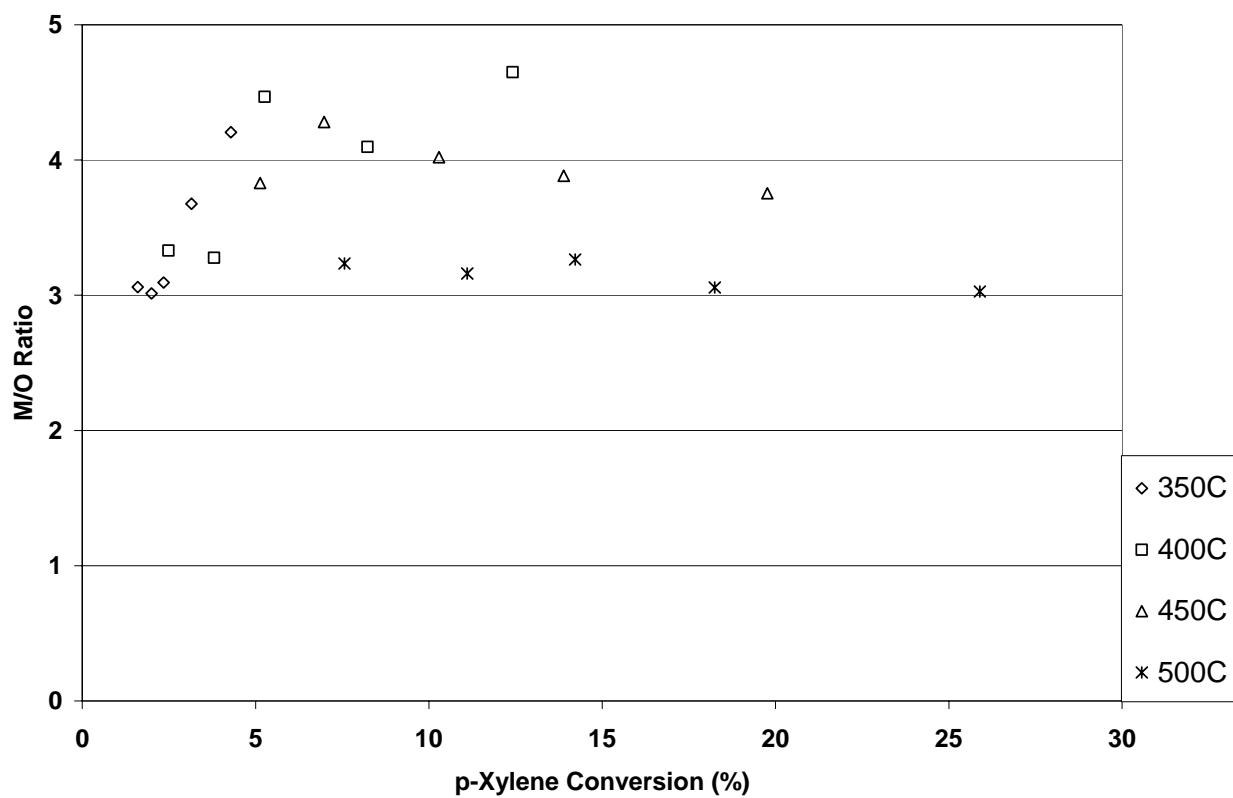


Fig.6. m-xylene/o-xylene (M/O) ratios vs. p-xylene conversion at different reaction temperatures

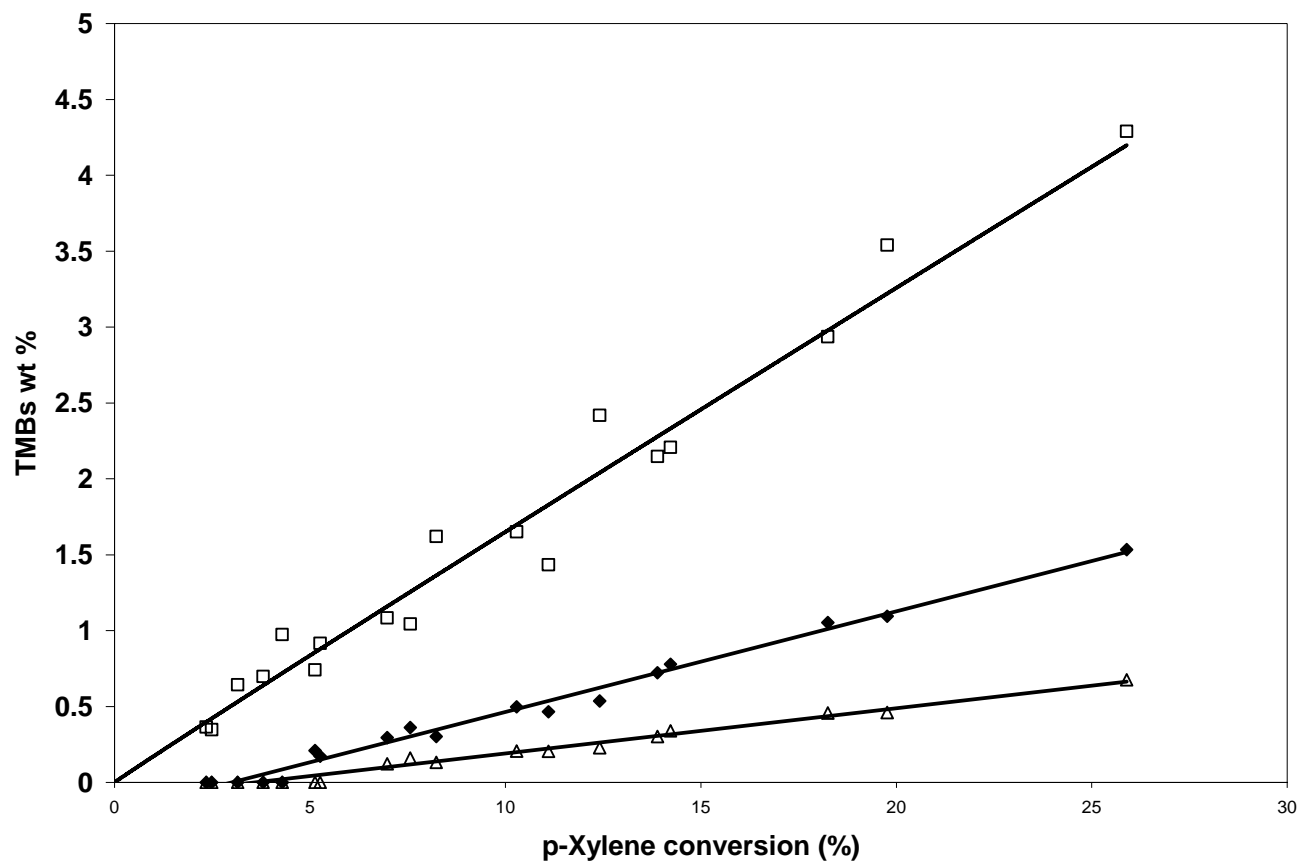


Fig.7. Distributions of trimethylbenzenes isomers as function of p-xylene conversion.  
 (Δ) 1,2,3-TMB, (□)1,2,4-TMB, (◆) 1,3,5- TMB

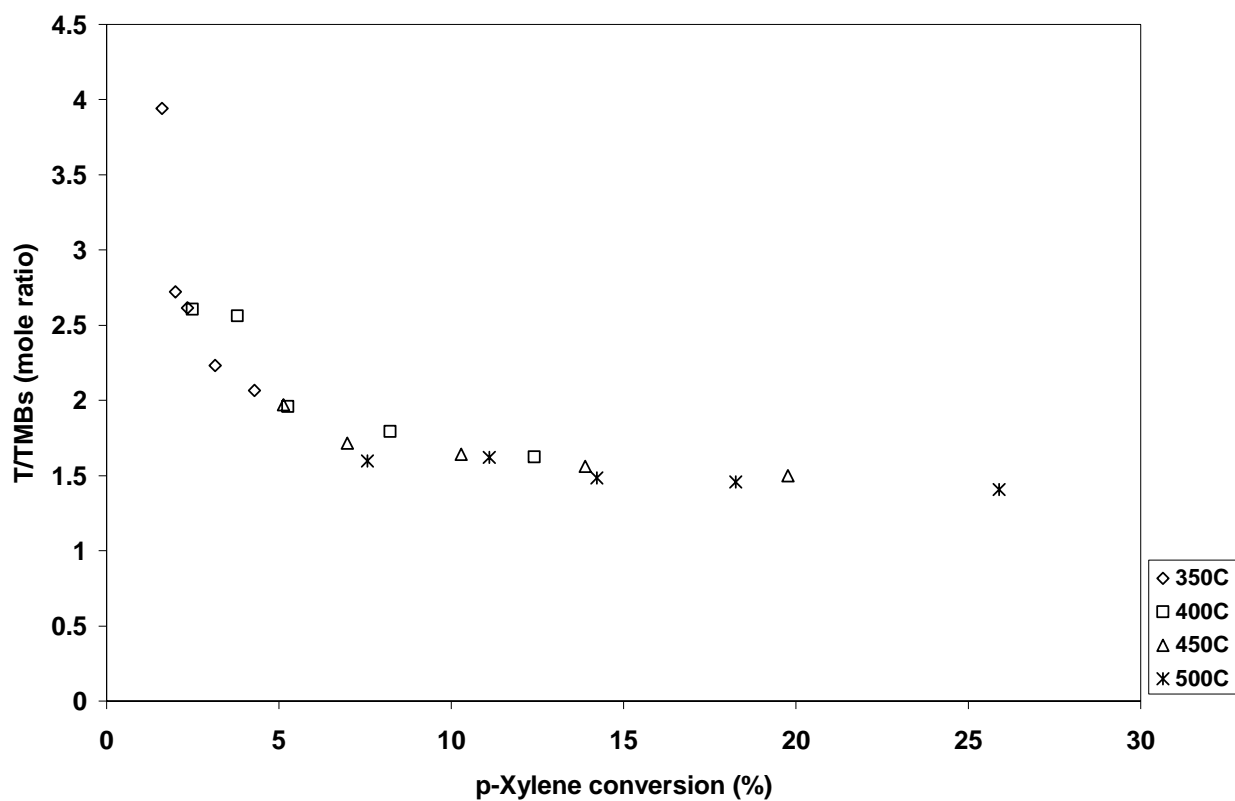


Fig. 8. Molar ratio of toluene to trimethylbenzenes as a function of p-xylene conversion at different reaction temperatures

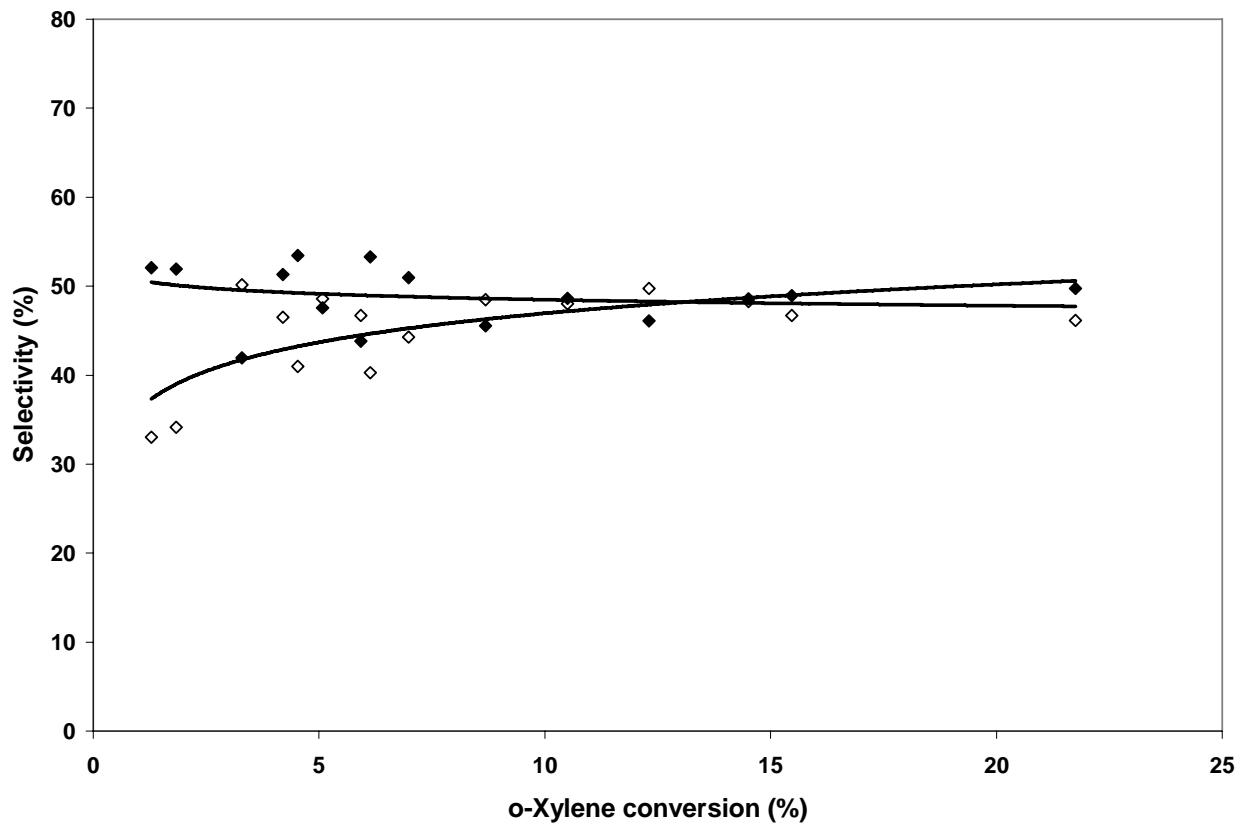


Fig.9. Isomerization and disproportionation selectivity during the transformation of o-xylene as function of o-xylene conversion. (◇) isomerization, (◆) disproportionation

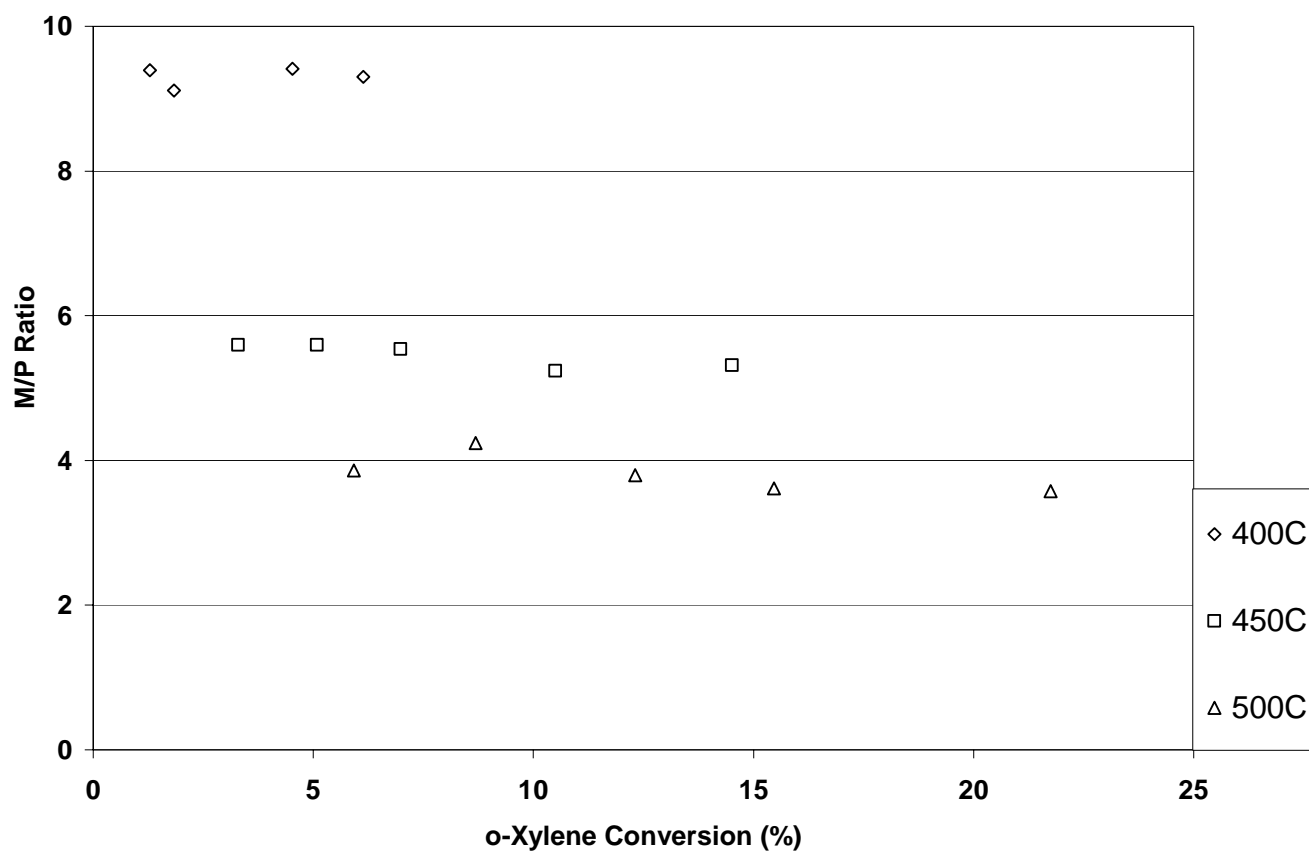


Fig.10. m-xylene/p-xylene (M/P) ratios vs. o-xylene conversion at different temperatures

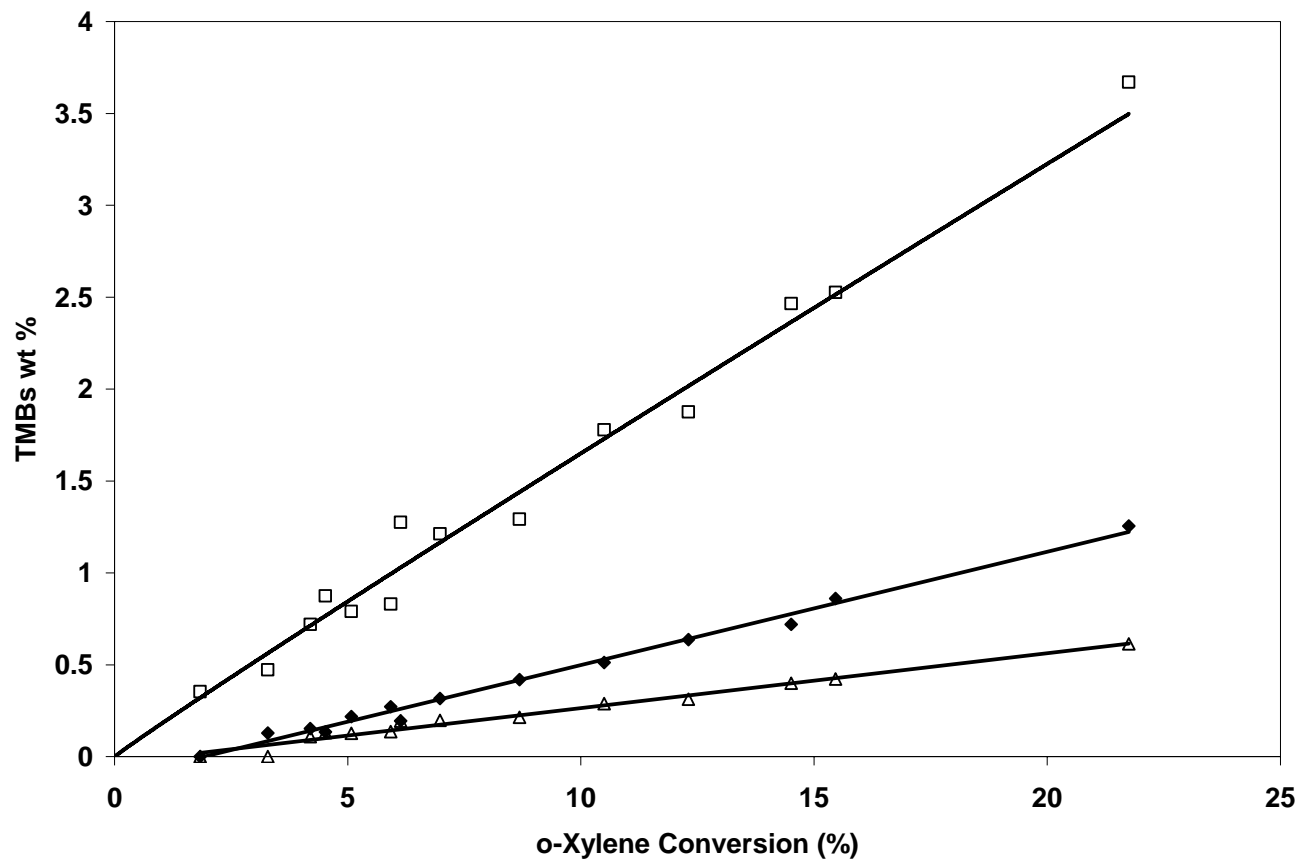


Fig.11. Distributions of trimethylbenzenes isomers as function of o-xylene conversion.  
 (Δ) 1,2,3-TMB, (□)1,2,4-TMB, (◆) 1,3,5- TMB



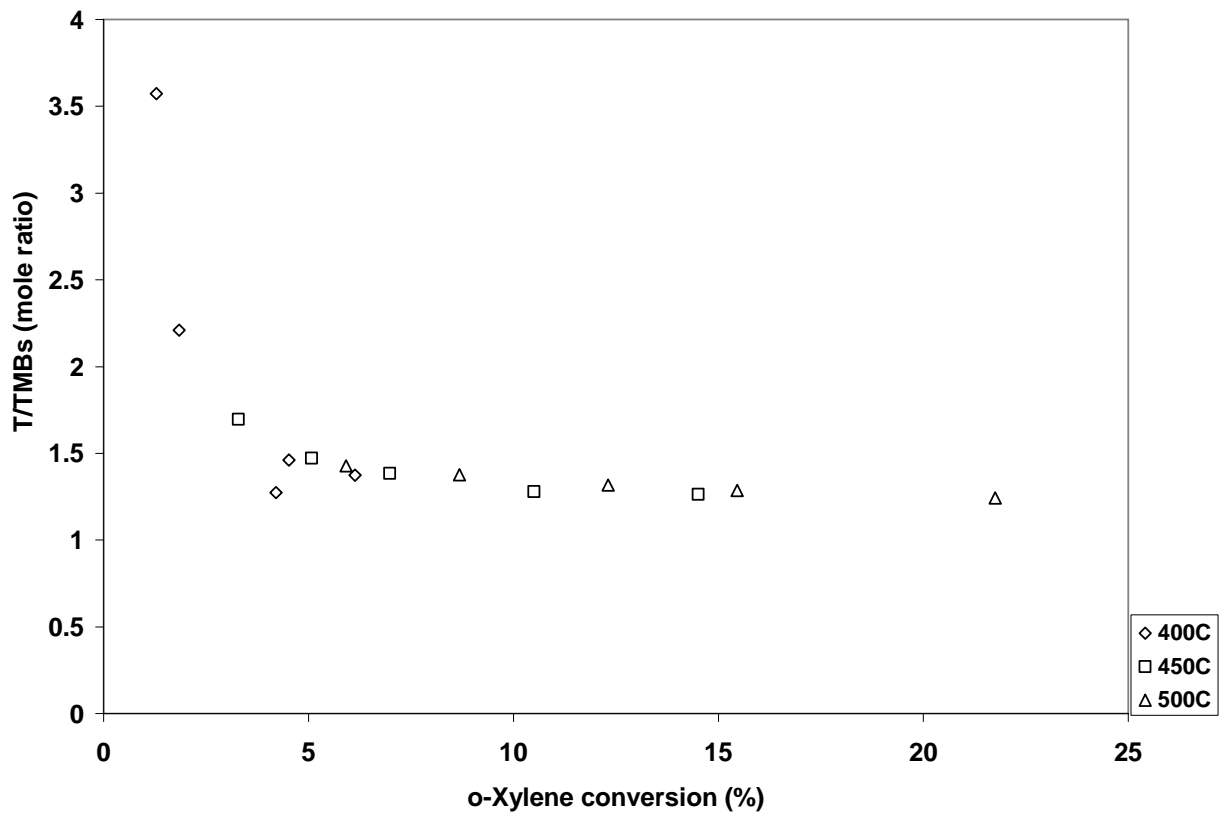


Fig. 12. Molar ratio of toluene to trimethylbenzene against o-xylene conversion at different reaction temperatures

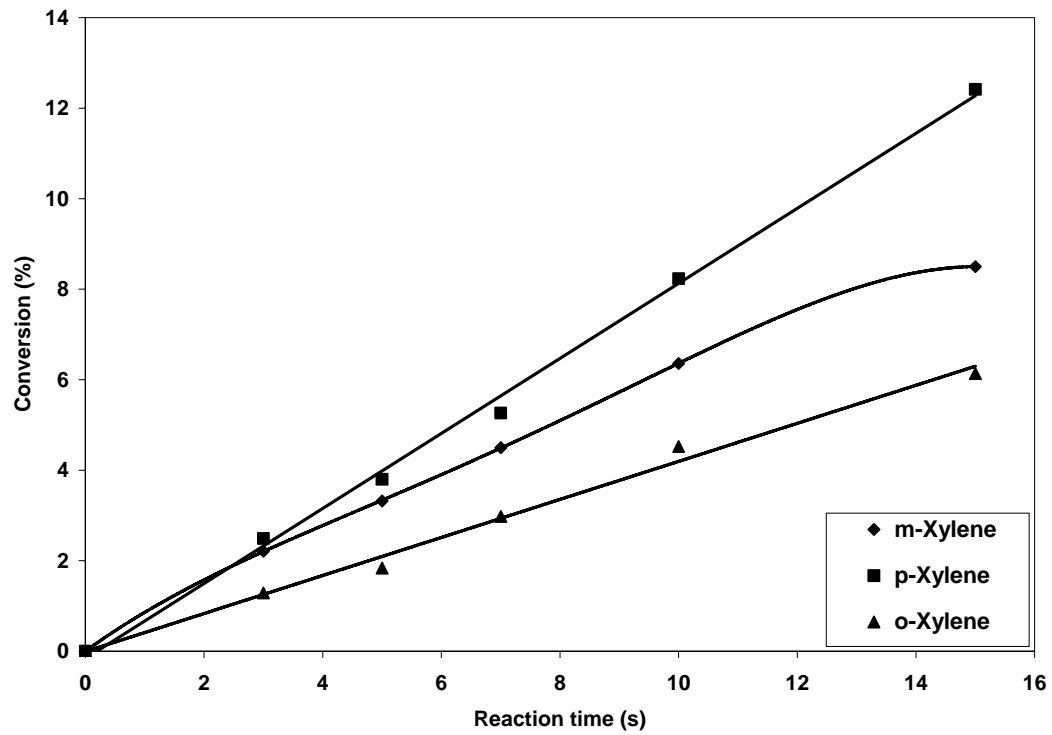


Figure 13. Xylenes conversion as a function of reaction time at 400°C

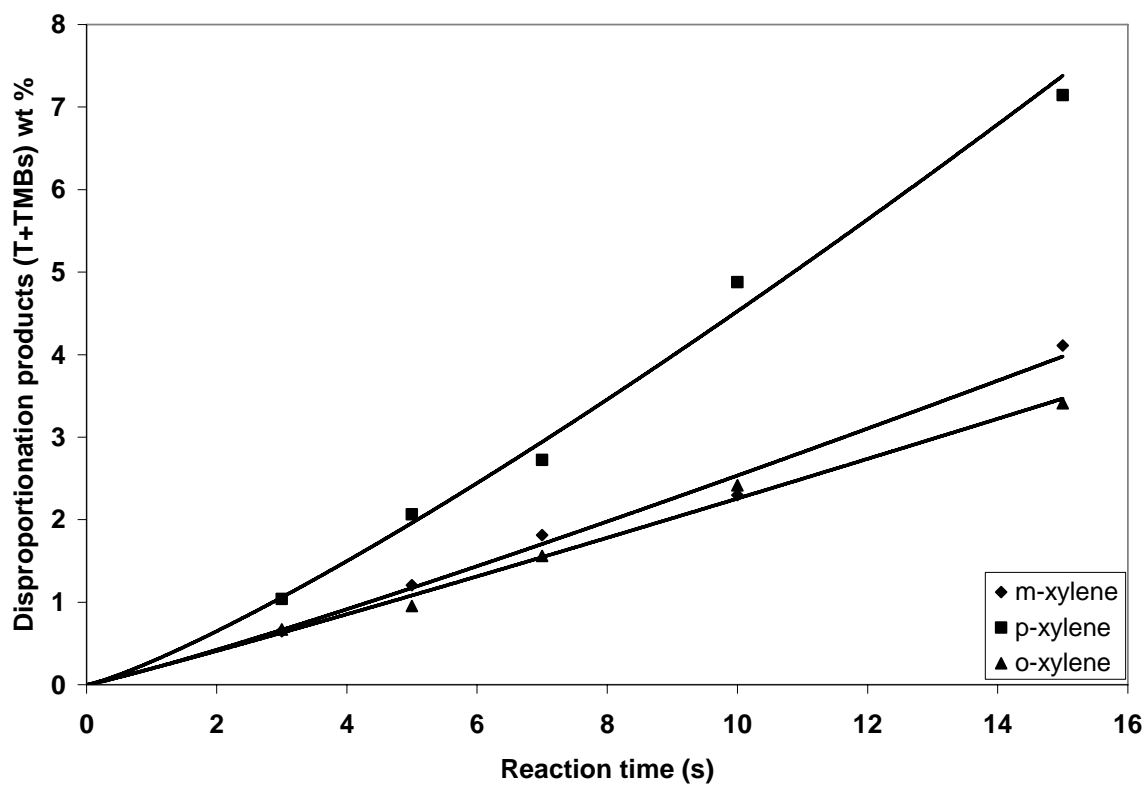


Fig.14. Comparison between the disproportionation products of the three xylene isomers at 400°C

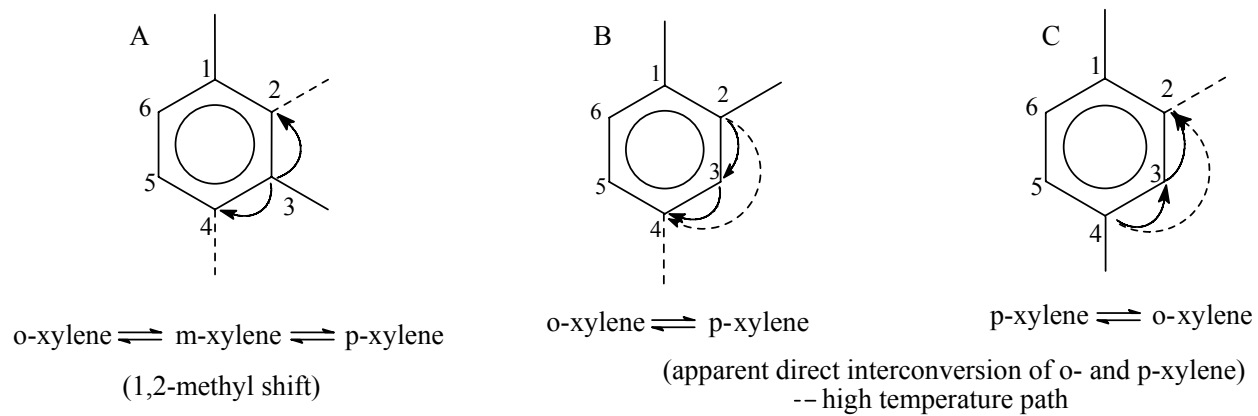
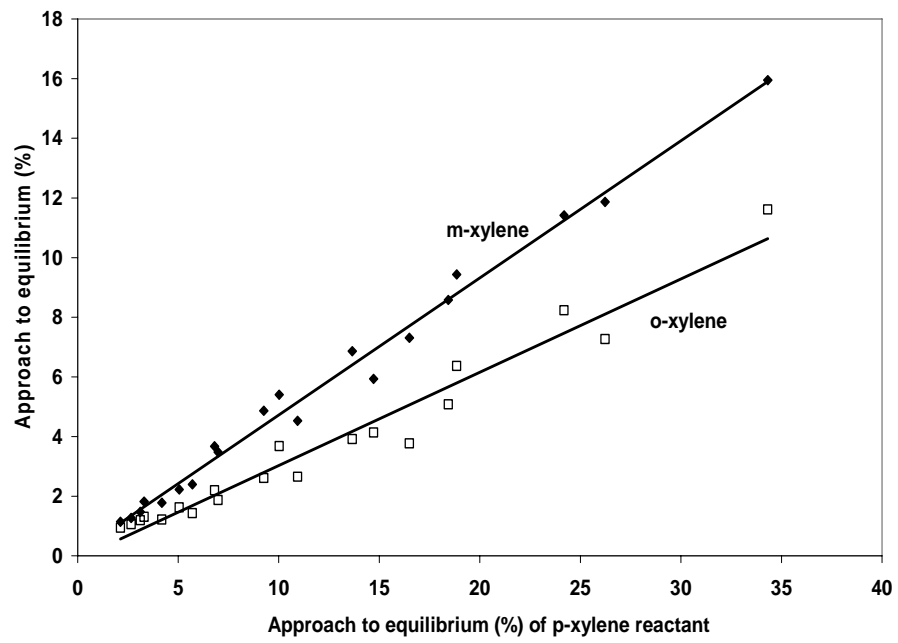
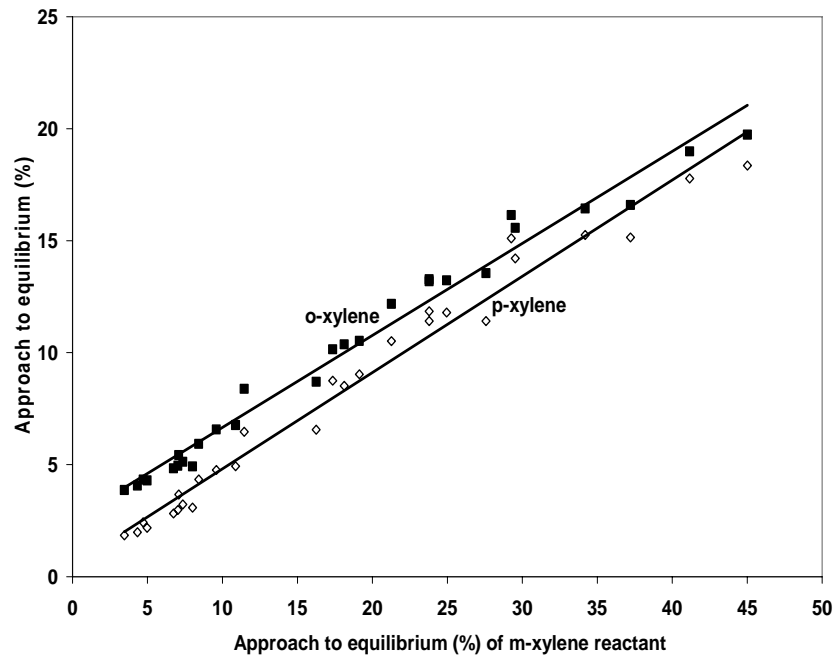


Fig. 15. Schematic representation of apparent methyl group migration during xylene transformation



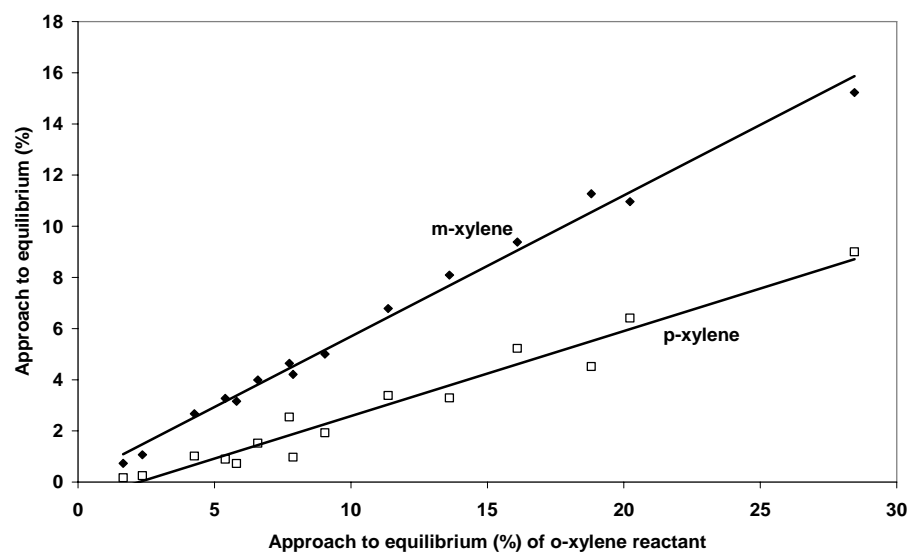


Figure 16. Approach to equilibrium composition (ATE) of the two xylene products as function of ATE of each xylene reactant.

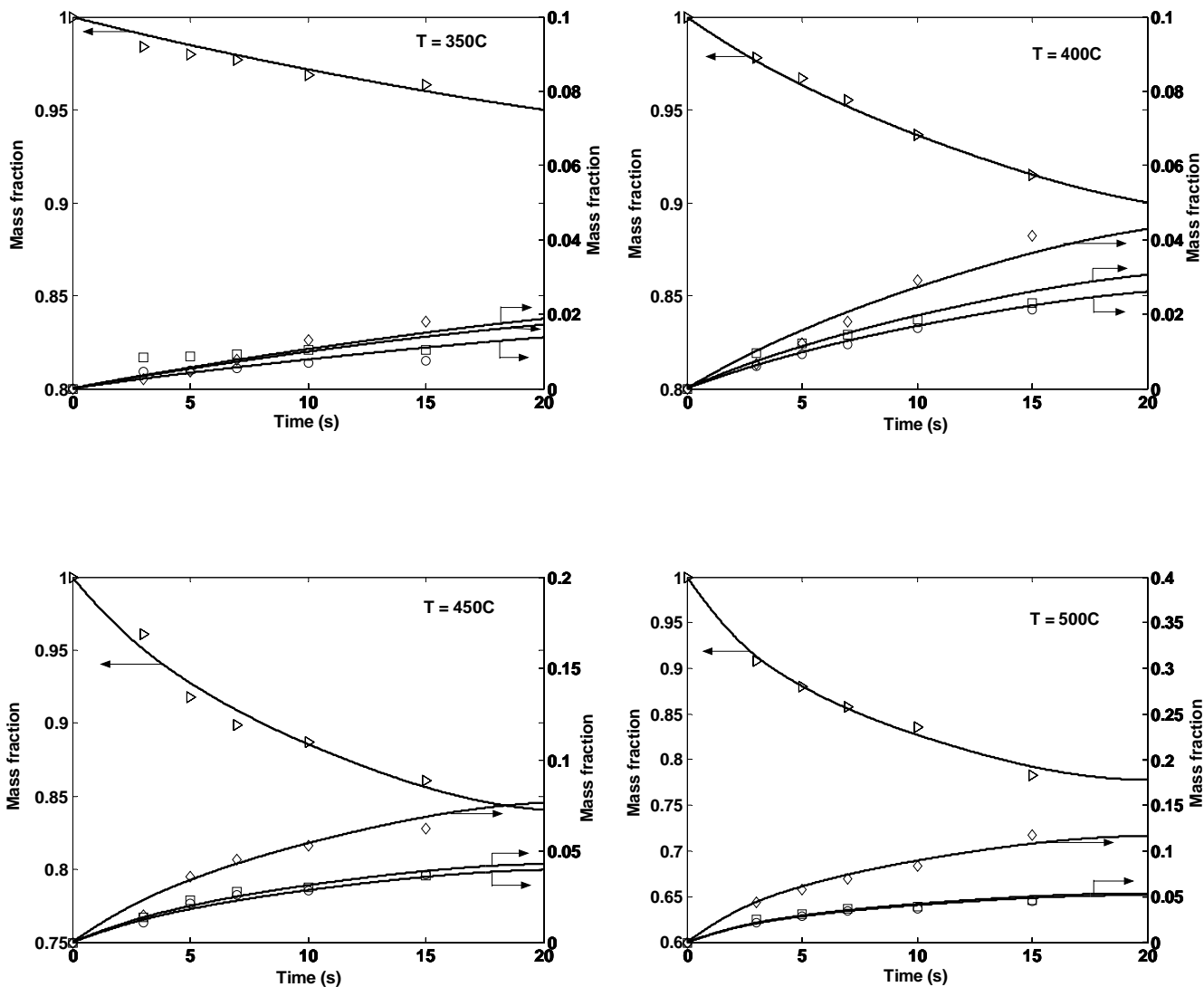


Figure 17. Comparison between experimental results and numerical simulations (—) based on overall m-xylene transformation (Scheme 1) ( $\circ$ ) p-xylene; ( $\square$ ) o-xylene; ( $\diamond$ ) T+TMBs; (tilted  $\Delta$ ) m-xylene.