

Catalytic Transformation of 1,3,5 -Trimethyl Benzene over USY Zeolite Catalyst

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Catalytic Transformation of 1,3,5-Trimethyl Benzene over USY Zeolite Catalyst

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Abstract

Catalytic transformation of 1,3,5-Trimethylbenzene (TMB) has been investigated over USY zeolite catalyst in a novel riser simulator at different operating conditions. The effect of reaction conditions on the variation of isomerization to disproportionation products ratio (I/D), distribution of trimethylbenzene (TMB) isomers, xylene/tetramethylbenzenes (X/TeMB) ratio and values of *p*-xylene/*o*-xylene (P/O) ratios are reported. Comparisons are made between the results of the 1,3,5-TMB and the earlier reported values of 1,2,4-TMB under similar conditions. Even though the kinetic diameters of these molecules slightly exceed the pore size of the USY zeolite (7.4Å), they still have access to the openings of the zeolite pore due to their flexibility. They are readily accommodated inside the zeolite channel system thereby allowing reaction to proceed. Surprisingly, *1,3,5-trimethylbenzene* was found to be more reactive than *1,2,4-trimethylbenzene* at temperatures above 450 °C and reaction times more than 5secs. The experimental results have been modeled using quasi-steady state approximation. Kinetic parameters for 1,2,4- and 1,3,5-TMB conversions into isomerization and disproportionation products were calculated using the catalyst activity decay function based on time on stream (TOS). The apparent activation energies were found to decrease as follows: $E_{135TMB, \text{disproportionation}} > E_{135TMB, \text{isomerization}} \approx E_{124TMB, \text{isomerization}} > E_{124TMB, \text{disproportionation}}$.

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Keywords: Trimethyl benzene, isomerization, disproportionation, fluidized-bed reactor, ZSM-5, USY-zeolite, modeling,

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1. Introduction:

The interest in the catalytic conversion of methyl aromatics comes from the fact that aromatics generally have wide applications in the petrochemical and chemical industries. Among aromatics, benzene, toluene and xylenes (BTX) are the three basic materials for most intermediates of aromatic derivatives¹. These base chemicals are practically produced by converting lower value toluene and trimethylbenzenes (TMB) coming from the reforming and pyrolysis of gasoline, into benzene and xylenes via disproportionation and transalkylation reactions. These processes offer a way to utilize the low cost toluene and TMB to produce much more attractive *p*-xylene product. In recent years, there have been efforts to find cost effective disproportionation and transalkylation catalytic processes to improve BTX production.

Trimethylbenzene transformations have been investigated over medium-pore zeolites like ZSM-5 and large-pore zeolites such as Y, Beta, and also mordenite. Collins *et al.*² investigated the transformation (isomerization and disproportionation) of trimethylbenzenes (TMBs) over LaY catalysts. In the disproportionation reaction, the transfer of one methyl group from TMBs led to the formation of equal amounts of xylene and tetramethylbenzene (TeMB) isomers. The authors reported that disproportionation appeared to be linearly related to the total conversion over most of the conversion range studied for both 1,2,4- and 1,3,5-TMB, whereas, for 1,2,3-TMB, isomerization was much more favored than disproportionation.

Cejka *et al.*³ studied the effect of the structure of large pore zeolites of beta, Y, L and Mordenite on TMB disproportionation. They concluded that zeolite beta and zeolite Y exhibit the highest stability in conversion of trimethylbenzenes. They also measured the diffusion coefficients of 1,2,4- and 1,3,5-TMBs and 1,2,3,5-TeMB at 25 and 100°C over zeolites Y, beta, and mordenite, and the measured values followed the decreasing order of *m*-xylene \gg 1,2,4-TMB > 1,3,5-TMB \approx TeMB. Wang *et al.*⁴ used zeolite beta to investigate its potential in xylene production reactions, including toluene disproportionation, TMB disproportionation, and toluene-TMB transalkylation. They found that the zeolite beta has excellent stability and transalkylation selectivity. The authors also demonstrated that xylene selectivity could be increased by blending toluene into feedstocks during the TMB disproportionation reaction.

Over medium pore zeolites, TMB transformations revealed much lower yield of xylenes compared to that under large pore and high acidity zeolites⁵⁻⁸. Roger *et al.*⁷ studied the conversion of 1,2,4-TMB over HZSM5. They observed that isomerization of 1,2,4-TMB to 1,2,3- and 1,3,5-TMB isomers was found to be the most rapid reaction with about 90%

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selectivity at low conversion and 1,2-methyl-shift was shown to take place on the external surface of the zeolite crystals. They noted that the disproportionation of 1,2,4-TMB was followed by rapid paring dealkylation of the TeMBs. The bulky intermediates (TeMBs) that reinforced the diffusional resistances by pore mouth narrowing favored the paring reaction inside the zeolite crystals.

Chu and Chen⁹ investigated the reactions of 1,3,5-TMB over beta zeolites in a fixed bed with various SiO₂/Al₂O₃ ratios. They found the conversion of 1,3,5-TMB decreasing gradually with an increase in the SiO₂/Al₂O₃ ratio which correlates very well with the number of acid sites which decreases with increasing SiO₂/Al₂O₃ of the zeolite. Their studies also showed that low SiO₂/Al₂O₃ zeolites favor the disproportionation reaction and high SiO₂/Al₂O₃ zeolites favor the isomerization reaction.

1,3,5-TMB has been reported by Pariente¹⁰ to directly disproportionate to *m*-xylene and 1,2,3,5-tetramethylbenzene (TeMB) via bimolecular transition state mechanism. The product of 1,2,3,5-TeMB may further isomerizes to 1,2,4,5-TeMB and 1,2,3,4-TeMB. On the other hand, 1,3,5-TMB isomerizes to 1,2,4-TMB and then undergo disproportionation to xylene isomers and TeMB isomers. The other possible reaction is dealkylation of 1,3,5-TMB to benzene, toluene, xylenes and light ends. In a related study, Yashima *et al.*¹¹ found that trimethylbenzene isomers were reactive in the order of 1,2,4-TMB > 1,2,3-TMB > 1,3,5-TMB over H-mordenite which was explained to be due to the molecular shape of TMB isomers.

Almost all of the research on the TMB transformations has been carried out in fixed bed reactors²⁻¹¹. Fluidized bed on the other hand reveals the importance of diffusional effects in these reactions. Atias *et al.*¹² investigated the conversion of 1,2,4-TMB in a riser simulator using USY zeolite catalysts under relevant FCC conditions. Their results showed that 1,2,4-TMB underwent both isomerization and disproportionation. The authors also modeled the kinetic reactions using both time-on-stream and reactant-converted (RC) models. They determined the intrinsic kinetic parameters for both isomerization and disproportionation reactions.

Al-Khattaf¹³ studied the effect of Y-zeolite acidity on reactions of 1,2,4-TMB in a riser simulator. He concluded that coke and gases were not produced over the low acidity catalyst, and only two reactions; isomerization and disproportionation are favored. On the other hand, high acidity catalyst produces huge amounts of gases and coke which are an indication of paring reactions

The aim of this study is to investigate the catalytic transformation reaction of 1,3,5-TMB over Y-zeolite type catalyst (FCC-Y) in a fluidized-bed reactor. The study will focus

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3 on the effect of reaction conditions (time, temperature, and conversion) on isomerization to
4 disproportionation products ratio (I/D), distribution of trimethylbenzene (TMB) isomers,
5 xylene/tetramethylbenzenes (X/TeMB) ratio and values of *p*-xylene/*o*-xylene (P/O) ratios
6 Comparisons will also be made with our earlier reported studies on catalytic transformations
7 of 1,2,4-TMB^{13,14}. An attempt will also be made to compare and contrast between the kinetic
8 modeling results of the two molecules.
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13 14 15 2. Experimental Procedure

16 17 2.1 *The Riser Simulator*

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19 All the experimental runs were carried out in the Riser Simulator. This reactor is a
20 novel bench scale equipment with internal recycle unit invented by de Lasa¹⁵. The Riser
21 Simulator consists of two outer shells, the lower section and the upper section which allow to
22 load or to unload the catalyst easily. The reactor was designed in such way that an annular
23 space is created between the outer portion of the basket and the inner part of the reactor shell.
24 A metallic gasket seals the two chambers with an impeller located in the upper section. A
25 packing gland assembly and a cooling jacket surrounding the shaft provide support for the
26 impeller. Upon rotation of the shaft, gas is forced outward from the center of the impeller
27 towards the walls. This creates a lower pressure in the centre region of the impeller thus
28 inducing flow of gas upward through the catalyst chamber from the bottom of the reactor
29 annular region where the pressure is slightly higher. The impeller provides a fluidized bed of
30 catalyst particles as well as intense gas mixing inside the reactor. A detailed description of
31 various Riser Simulator components, sequence of injection and sampling can be found in
32 Kraemer¹⁶.
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45 46 2.2 *Materials*

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48 Ultrastable Y zeolite (USY) was obtained from Tosoh Company. The Na-zeolite was
49 ion exchanged with NH₄NO₃ to replace the sodium cation with NH₄⁺. Following this, NH₃
50 was removed and the H form of the zeolite was spray-dried using kaolin as the filler and
51 silica sol as the binder. The resulting 60-μm catalyst particles had the following composition:
52 30 wt% zeolite, 50 wt% kaolin, and 20 wt% silica sol. The process of sodium removal was
53 repeated for the pelletized catalyst. Following this, the catalyst was calcined for 2 hr at
54 600°C. Finally, the fluidizable catalyst particles (60-μm average size) were treated with
55 100% steam at 760°C for 5 hr forming FCC-Y catalyst used in our studies.
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3 Analytical grade (99% purity) pure 1,3,5- and 1,2,4-trimethylbenzenes were obtained
4 from Sigma-Aldrich. All chemicals were used as received as no attempt was made to further
5 purify the samples.
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8 9 10 2.3 Procedure

11 Regarding the experimental procedure in the Riser Simulator, 0.81g of catalyst was
12 weighed and loaded into the Riser Simulator basket. The system was then sealed and tested
13 for any pressure leaks by monitoring the pressure changes in the system. Furthermore, the
14 reactor was heated to the desired reaction temperature. The vacuum box was also heated to
15 around 250°C and evacuated to around 0.5psi to prevent any condensation of hydrocarbons
16 inside the box. The heating of the Riser Simulator was conducted under continuous flow of
17 inert gases (argon) and the process usually takes few hours until thermal equilibrium is
18 finally attained. Meanwhile, before the initial experimental run, the catalyst was activated for
19 15 minutes at 620°C in a stream of air. The temperature controller was set to the desired
20 reaction temperature, in the same manner the timer was adjusted to the desired reaction time.
21 At this point the GC is started and set to the desired conditions.
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31 Once the reactor and the gas chromatograph have reached the desired operating
32 conditions, the feed stock was injected directly into the reactor via a loaded syringe. After the
33 reaction, the four port valve immediately opens ensuring that the reaction was terminated and
34 the entire product stream sent on-line to the analytical equipment via a pre-heated vacuum
35 box chamber. The products were analyzed in an Agilent 6890N gas chromatograph with a
36 flame ionization detector and a capillary column INNOWAX, 60-m cross-linked methyl
37 silicone with an internal diameter of 0.32 mm.
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43 The reactant injection was carried out at atmospheric pressure. Subsequently, the
44 pressure increases upon reactant vaporization. The reaction pressure of the system after
45 reactant vaporization was about 2.0-2.5 atm. However, the reaction period develops at
46 essentially constant pressure. This is equivalent to having total constant pressure since the
47 total number of moles remains constant.
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53 54 3. Results and Discussion

55 Catalytic experiments were carried out in the riser simulator at catalyst/reactant ratio
56 of 5 (weight of catalyst = 0.81g, weight of reactant injected = 0.162g); residence times of 3,
57 5, 7, 10, 13 and 15 sec; and temperatures of 400, 450 and 500°C. During the course of the
58 investigation, a number of runs were repeated to check for reproducibility in the conversion
59 results, which was found to be excellent. Typical errors were in the range of $\pm 2\%$.
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3.1 Catalyst Characterization

The BET surface area was measured according to the standard procedure ASTM D-3663, using NOVA 1200 unit (QUANTA CHROME). The acid property of the catalyst was characterized by NH₃ temperature-programmed desorption (NH₃-TPD). In all the experiments, 50 mg of sample was outgassed at 400°C for 30 min in flowing He and then cooled down to 150°C. At that temperature, NH₃ was adsorbed on the sample by injecting pulses of 2 µl/pulse. The injection was repeated until the amount of NH₃ detected was the same for the last two injections. After the adsorption of NH₃ was saturated, the sample was flushed at 150°C for 1 h with He to remove excess NH₃, and then the temperature was programmed at 30 °C/min up to 1000°C in flowing He at 30 ml/min. Flame ionization detector was used to monitor the desorbed NH₃. The results of the catalyst characterization are summarized in **Table 1**.

3.2 1,2,4-Trimethylbenzene Transformation Reactions

The results of transformation reaction of 1,2,4-TMB over FCC-Y at different reaction temperatures and contact times have also been reported by Al-Khattaf *et al.*^{13,14}. The product distribution is partially reproduced in **Table 2**. The experimental results showed that 1,2,4-TMB conversion increases with both reaction time and temperature with conversion of up to 38% observed at 15sec and reaction temperature of 500°C.

3.3 1,3,5-Trimethylbenzene Transformation Reactions

Results of the transformation reaction of 1,3,4-TMB over FCC-Y at different reaction temperatures and contact times are presented in a **Table 3**. **Figure 1** depicts that 1,3,5-TMB conversion increases with both reaction time and temperature. The experimental results (see **Table 3**) show that isomerization, disproportionation, and transalkylation reactions are taking place. The disproportionation reaction involves the formation of xylenes and tetramethylbenzenes (TeMBs) from two molecules of 1,3,5-TMB. Subsequently, the xylenes (one of the disproportionation product) react with the TMB to form a transalkylation product toluene. Xylene yields are shown in **Figure 2** at different temperatures. It is shown in this figure that xylene yields increase with conversion and that they are less sensitive to the temperature increment. Toluene was also detected in the product but in small amounts as shown in **Table 3**. For the reaction of 1,3,5-TMB over Y-zeolite, toluene is proposed to be a secondary product formed by the disproportionation of xylenes. Since negligible amount of gases was observed, it cannot be concluded that toluene is produced as a result of

dealkylation of 1,3,5-TMB to benzene, toluene, xylenes and light ends. It has been reported that 1,3,5-TMB directly disproportionate to *m*-xylene and 1,2,3,5-tetramethylbenzene (TeMB) via bimolecular transition state mechanism. The product of 1,2,3,5-TeMB may then further isomerizes to 1,2,4,5-TeMB and 1,2,3,4-TeMB. On the other hand, 1,3,5-TMB isomerizes to 1,2,4-TMB and then undergo disproportionation to xylene isomers and TeMB isomers¹⁰.

The data from the isomerization reaction show that the isomerization yield (both 1,2,4-TMB and 1,2,3-TMB) increases with both conversion and reaction temperature (see **Figure 3**). However, higher amounts of 1,2,4-TMB were found as compared to the 1,2,3-TMB. Regarding the second disproportionation product TeMBs, **Figure 4** shows that the yield of TeMBs increases also with both conversion and temperature for FCC-Y. Furthermore, three different isomers of tetramethylbenzenes (TeMBs) were detected (1,2,4,5-TeMB, 1,2,3,5-TeMB, and 1,2,3,4-TeMB). Benzene and pentamethylbenzene (PeMB) have not been found in the reaction mixture.

On the basis of the results presented in **Figures 2 & 4**, it can be concluded that xylenes and TeMB are primary products of the 1,3,5-TMB transformation reaction. This is because their respective yields extrapolate to the origin (i.e. zero yield at zero conversion). This is contrary to the findings of Pariente¹⁰ who reported that 1,3,5-TMB first isomerizes to 1,2,4-TMB and then undergo disproportionation to xylene isomers and TeMB isomers.

1,3,5-TMB can simultaneously undergo isomerization and disproportionation reactions. **Figure 5** shows that the disproportionation to isomerization (D/I) ratio is around 1.25 at all conversion levels over the FCC-Y catalyst. This indicates that 1,3,5-TMB preferentially undergoes disproportionation as compared to isomerization (approximately 1.25 times greater) over the FCC-Y catalyst. The data also show that the effect of temperature and conversion on the D/I ratio is not very significant. The main reason for the higher disproportionation rate over zeolite compared to the isomerization rate is that while the isomerization reaction can take place only over Brønsted acid sites, disproportionation reaction can occur over both Lewis and Brønsted sites.¹⁷

3.4 1,3,5-TMB versus 1,2,4-TMB

3.4.1 Reactivity

Conversions of 1,3,5-TMB and 1,2,4-TMB are plotted against reaction time in **Fig. 6a & b** at 400°C and 500°C respectively. The plots show that 1,3,5-TMB is more reactive at temperatures above 450°C and reaction times greater than 5 secs. 1,3,5-TMB reached a

conversion of 43.9% at 15sec and reaction temperature of 500°C, while 1,2,4-TMB conversion of up to 38% was observed at the same condition. This result was obtained despite the fact that 1,2,4-TMB with a smaller size has a diffusion advantage over the 1,3,5-TMB isomer. Yashima *et al.*¹¹ reported the reactivity of trimethylbenzene isomers to decrease in the order of 1,2,4-TMB > 1,2,3-TMB > 1,3,5-TMB over H-mordenite.

3.4.2 Xylene Yield

Xylene yields in wt% were plotted versus conversion for both 1,3,5- and 1,2,4- **Figs. 7a & b** over the FCC-Y catalyst. From the plots, it is observed that 1,2,4-TMB consistently gave higher xylene yield than 1,3,5-TMB at all temperatures studied when compared at similar conversions. It is important to note that the xylene yields in this study are smaller than those reported over zeolite beta^{4,9} where higher levels of conversions were reported.

3.4.3 *p*-Xylene to *o*-Xylene (P/O) ratio

The ratios of *para*- to *ortho*-xylene (P/O) in the product mixture are presented in **Figs. 8a & b** for the two TMB molecules. The P/O ratio for the 1,3,5-TMB averages 0.75 at 400°C, and 0.82 at 500°C over the whole conversion range. While for the 1,2,4-TMB, the ratio is close to 0.70 at 400°C and 0.77 at 500°C. The results generally show that 1,3,5-TMB posted relatively higher ratios of *para*- to *ortho*-xylene than 1,2,4-TMB at all temperatures, and in the entire conversion range. Jones *et al.*¹⁸ reported that large pore zeolites such as the one under study where it is highly likely that bimolecular mechanism operates, P/O ratios below the thermodynamic ratio of approximately 1 are possible.

3.4.4 Distribution of TMB isomers

The molecular size of 1,3,5-TMB (8.6Å) is the largest among the three isomers, followed by the 1,2,3-isomer and then 1,2,4-isomer. Usually, zeolites with large cages generally should favor the formation of the larger TMB molecule, while small pore zeolites favor the smaller TMB isomer. Experimental results for the 1,3,5-TMB transformation (**Table 3**) have shown that higher amounts of 1,2,4-TMB were found as compared to the 1,2,3-TMB. Similarly, the results of 1,2,4-TMB (**Table 2**) show that the yield of 1,3,5-TMB is greater than that of the 1,2,3-isomer. These results point to the fact that shape selectivity plays an important role in this reaction.

Figs. 9a & b show the distribution of either 1,2,4-TMB/1,2,3-TMB or 1,3,5-TMB/1,2,3-TMB versus conversion for 1,3,5- and 1,2,4-TMB molecules respectively. The ratio of the 1,2,4- to the 1,2,3-isomer formed over FCC-Y during the transformation of 1,3,5-

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TMB is about 8.1 at 400°C and decreases to 7.0 at 500°C, and was found to be invariant with conversion. At both temperatures, catalyst FCC-Y gave a 1,3,5-TMB/1,2,3-TMB ratio of about 2.1 for the 1,2,4-TMB transformation at all experimental conditions. This indicates that ratio of 1,2,4-to 1,2,3-isomers formed during 1,3,5-TMB transformation is approximately 4 times the ratio of 1,3,5- to 1,2,3-TMB formed during the transformation of 1,2,4-TMB.

Chu and Chen⁹ had a 1,2,4-/1,2,3-trimethylbenzene ratio of about 10.5 that decreased to 7.5 for a temperature range of 220-470 °C over zeolite beta. Wang *et al.*⁴ reported a value of 2.7 for the 1,3,5-/1,2,3-trimethylbenzene ratio at 348°C over USY-zeolite, while Park and Rhee⁸ reported the ratio of 1,3,5-/1,2,3-TMB as 1.99 over HNU-87 (a zeolite with catalytic properties falling between those of medium- and large-pore zeolites).

3.4.5 Xylene to Tetramethylbenzenes ratio

Figs. 10a & b show xylene-to-tetramethylbenzene (X/TeMB) distributions at various conversion levels over the FCC-Y catalyst. In the absence of secondary transalkylation or dealkylation, the molar ratio of xylene-to-tetramethylbenzene (X/TeMB) should be unity. However, it can be seen in these figures that the xylenes/TeMBs ratio is higher than the stoichiometric ratio of 1.0. The X/TeMB ratio for both the two molecules is on the average 1.4 over the entire conversion range. This is in agreement with the results of Atias *et al.*¹² who found increased amounts of xylenes over TeMBs. The higher ratio of xylenes/TeMBs indicates that either secondary transalkylation or dealkylation reactions are taking place. The dealkylation reaction was found to be inconsequential due to the very small amount of gases observed. TeMBs may then have been trapped in micropores as coke precursors to account for the excess xylenes in relation to TeMBs, or it may be attributed to the higher desorption rates of xylenes as compared to tetramethylbenzenes.

3.4.6 Disproportionation to Isomerization (D/I) ratio

1,3,5-TMB consistently gave higher isomerization yields compared to 1,2,4-TMB (**Fig. 11**). On the other hand, 1,2,4-TMB produced more disproportionation products than the 1,3,5-TMB molecule as shown in **Fig. 12**. This tend to indicate that the energy of activation for isomerization for 1,3,5-TMB should be lower than that of 1,2,4-TMB, while its is the opposite for the energy of activation for disproportionation. This has been proved to be true based on the modeling results presented in section 4.

Figs. 13a & b show disproportionation to isomerization ratios calculated at various conversions over the FCC-Y catalyst. 1,3,5-TMB shows a disproportionation to isomerization (D/I) ratio of around 1.25 at all conversion levels over the FCC-Y catalyst. The

D/I for 1,2,4-TMB lies between 2.5-3.0. These results indicate both the two molecules preferentially undergo disproportionation as compared to isomerization over the FCC-Y catalyst, approximately 1.25 times greater for the 1,3,5-TMB, and 2.5-3.0 for the 1,2,4-TMB. The data also show that the effect of temperature and conversion on the D/I ratio is not very significant.

4. Kinetic Modeling

4.1 Model Formulation

The experimental results were modeled using steady state approximations with catalyst decay to be function of time on stream. The kinetic model representing the overall transformation of the two TMB molecules is based on isomerization and disproportionation reactions only. The reaction network shown in scheme 1 was used.



Scheme 1

The following set of species balances and catalytic reactions can be written:

$$\frac{V}{W_c} \frac{dC_{TMB}}{dt} = -[k_{iso} C_{TMB} + 2k_{disp} C_{TMB}^2] \exp[-\alpha t] \quad (1)$$

$$\frac{V}{W_c} \frac{dC_{iso}}{dt} = k_{iso} C_{TMB} \exp[-\alpha t] \quad (2)$$

$$\frac{V}{W_c} \frac{dC_{disp}}{dt} = k_{disp} C_{TMB}^2 \exp[-\alpha t] \quad (3)$$

Where C_{TMB} , 1,2,4- or 1,3,5-TMB concentration in the riser simulator; V , volume of the riser (45 cm³); W_c , mass of the catalysts (0.81 gcat); t , time (sec); α , deactivation constant; k , rate constant (cm³/gcat.sec).

It should be noted that the following assumptions were made in deriving the reaction network:

1. The isomerization of 1,2,4-TMB follow simple first-order, whereas disproportionation is second order as proposed by Atias *et al.*¹² and Ko and Kuo¹⁹.
2. An irreversible reaction path is assumed for both the isomerization and disproportionation reaction.
3. Tetramethylbenzenes are entirely the results of the disproportionation reaction. [The disproportionation reaction involves the formation of 1 mole of Xylenes and 1 mole of tetramethylbenzenes from 2 moles of 1,2,4-TMB]
4. The model assumes catalytic reactions only and neglects thermal conversion. This hypothesis of a negligible contribution from thermal reactions has been fully justified¹².
5. A single deactivation function defined for all the reactions taking place.
6. Dealkylation reaction is inconsequential due to the minor amounts of gases in the reaction system.
7. The reactor operates under isothermal conditions, justified by the negligible temperature change observed during the reactions.

Using similar derivation procedures outlined in Atias *et al.*¹², eqs 1-3 can be expressed in terms of weight fractions which are the measurable variables from GC analysis as:

$$\frac{dy_A}{dt} = -[k_{iso}y_A + 2v_Ak_{disp}y_A^2] \frac{W_c}{V} \exp[-\alpha t] \quad (4)$$

$$\frac{dy_B}{dt} = v_I k_{iso} y_A \frac{W_c}{V} \exp[-\alpha t] \quad (5)$$

$$\frac{dy_C}{dt} = v_C k_{disp} y_A^2 \frac{W_c}{V} \exp[-\alpha t] \quad (6)$$

where A, B, and C represent the reactant, the reaction isomerization products, and the disproportionation product represented by xylenes, respectively. And,

$$v_A = \frac{W_{hc}}{MW_{TMB} V} \quad v_I = \frac{MW_{TMB}}{MW_{TMB}} = 1 \quad v_C = \frac{W_{hc} MW_{Xylene}}{MW_{TMB}^2 V}$$

where

W_{hc} = total mass of hydrocarbons inside the riser (0.162 g)

MW_X = molecular weight of X molecule

Kinetic constants for isomerization and disproportionation can be expressed using the Arrhenius equation, and a centering temperature, T_o is the average reaction temperature introduced to reduce parameter interaction.

$$k_i = k_{0,i} \exp\left(\frac{-E_i}{R} \left[\frac{1}{T} - \frac{1}{T_o}\right]\right) \quad (7)$$

4.2 Discussion of Kinetic Modeling Results

The kinetic parameters $k_{0,i}$, E_i , and α , for the reactions taking were obtained using non-linear regression (MATLAB package). **Table 4** reports the parameters obtained along with the corresponding 95% confidence limits for 1,3,5-TMB using time-on-stream model, the corresponding correlation matrix is presented in **Table 5**. From the results of the kinetic parameters presented in **Table 4**, it is observed that catalyst deactivation was found to be very small, $\alpha = 0.001$, indicating low coke. Apparent activation energies of 14.22 and 15.64 kJ/mol were obtained for the isomerization and disproportionation reaction of 1,3,5-TMB, respectively. The correlation matrix (**Table 5**) displayed low cross-correlation between the regressed parameters showing that the kinetic parameters are accurate.

Table 6 reports the parameters obtained for 1,2,4-TMB under similar conditions. The corresponding correlation matrix is given in **Table 7**. From the results, it can be concluded that catalyst deactivation was also small, $\alpha = 0.013$. Apparent activation energies of 14.31 and 10.07 kJ/mol were obtained for the isomerization and disproportionation reaction of 1,2,4-TMB, respectively.

The apparent energy of activation for isomerization for both molecules is similar (approx. 14.22 vs. 14.31 kJ/mol) with a slight advantage for the 1,3,5-TMB. However, 1,3,5-TMB's activation energy for disproportionation is greater than that of 1,2,4-TMB which is consistent with higher diffusion constraints of 1,3,5-TMB. Disproportionation reaction involves the formation of xylenes and tetramethylbenzenes (TeMBs) from two molecules of the TMB-isomer. This explains why D/I for 1,3,5-TMB (which is approximately 1.25) is lower than the D/I for 1,2,4-TMB that is between 2.5-3.0. The lower 1,2,4-TMB activation energy for disproportionation enable it to have higher disproportionation rate compared to the isomerization rate.

Atias *et al.*¹² reported an apparent energy of activation of 19.7 kJ/mol for the isomerization reaction of 1,2,4-TMB over USY zeolite, and a value of 6.7 kJ/mol for the

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disproportionation reaction. These values are in close agreement with the results of present study.

It can be observed from the modeling results that isomerization of 1,2,4-TMB involves a higher apparent energy of activation (E_{iso}) as compared to the disproportionation reaction (E_{disp}). This is in agreement with the findings of Atias *et al.*¹² in which the authors reported similar trend for the transformation reaction of 1,2,4-TMB over USY. On the other hand, apparent energy of activation for isomerization for the 1,3,5-TMB molecule is slightly lower than the disproportionation reaction energy. Molecular size plays an important role here as it is generally easier (less energy is required) for a bulky molecule to transform into a smaller molecule than the other way round.

5. Conclusions

The following conclusions can be drawn from the transformation reaction 1,3,5-TMB over the FCC-Y zeolite catalyst, and the subsequent comparison with the reactions of 1,2,4-TMB under similar conditions.

1. Even though the kinetic diameters of these molecules (8.6Å for 1,3,5-TMB and 7.6Å for 1,2,4-TMB) slightly exceed the pore size of the USY zeolite (7.4Å), they still have access to the openings of the zeolite pore due to their flexibility. They are accommodated inside the zeolite channel system thereby allowing reaction to proceed.

2. The results show that 1,3,5-trimethylbenzene transforms mainly via two reactions, isomerization and disproportionation over FCC-Y zeolite catalyst. The reaction mechanism is very much similar to that of 1,2,4-TMB. The results show that 1,3,5-TMB preferentially undergoes disproportionation as compared to isomerization (D/I ratio approximately 1.25) over the FCC-Y catalyst. While the D/I ratio for 1,2,4-TMB is between 2.5-3.0 consistent with its lower activation energy for disproportionation.

3. 1,3,5-TMB was found to be more reactive than 1,2,4-TMB at temperatures above 450°C and reaction times greater than 5 secs. This result was obtained despite the fact that 1,2,4-TMB with a smaller size has a diffusion advantage over the 1,3,5-TMB isomer.

4. The transformation reaction of 1,3,5-TMB consistently gave higher P/O ratio, higher TMB isomer distribution ratio, but lower xylene yield when compared to the 1,2,4-TMB reaction.

5. Kinetic parameters for the 1,3,5- and 1,2,4-TMB molecules during their transformation reactions isomerization and disproportionation products have been calculated using the catalyst activity decay function based on time on stream (TOS). The apparent

activation energies were found to decrease as follows: $E_{135TMB, \text{disproportionation}} > E_{135TMB, \text{isomerization}} \approx E_{124TMB, \text{isomerization}} > E_{124TMB, \text{disproportionation}}$.

Acknowledgments

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Nomenclature

C_i concentration of specie i in the riser simulator (mole/m³)

CL confidence limit

E_i apparent activation energy of i th reaction, kJ/mol

k apparent kinetic rate constant (m³/kgcat.s).

$$= k'_o \exp\left[\frac{-E_R}{R} \left(\frac{1}{T} - \frac{1}{T_o}\right)\right]$$

k'_o Pre-exponential factor in Arrhenius equation defined at an average temperature [m³/kgcat.s], units based on first order reaction

MW_i molecular weight of specie i

r correlation coefficient

R universal gas constant, kJ/kmol K

t reaction time (s).

T reaction temperature, K

T_o average temperature of the experiment

V volume of the riser (45 cm³)

W_c mass of the catalysts (0.81 gcat)

W_{hc} total mass of hydrocarbons injected in the riser (0.162 g)

y_i mass fraction of i th component (wt%)

Greek letters

α apparent deactivation constant, s⁻¹ (TOS Model)

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- Table 1: Characterization of used USY Zeolite Catalysts
- Table 2: Product distribution (wt %) at various reaction conditions for the *1,2,4-Trimethylbenzene* transformation reactions
- Table 3: Product distribution (wt %) at various reaction conditions for *1,3,5-Trimethylbenzene* transformation reactions
- Table 4: Estimated Kinetic Parameters Based on Time on Stream (TOS Model) –1,3,5-TMB
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Table 1
Characterization of used Catalyst

| Catalyst | Acidity (mmol/g) | BET Surface Area (m ² /g) | Crystallite size (μm) | Unit cell size (Å) | SiO ₂ /Al ₂ O ₃ (mol/mol) | Na ₂ O wt % |
|----------|------------------|--------------------------------------|-----------------------|--------------------|--|------------------------|
| FCC-Y | 0.033 | 155 | 0.9 | 24.27 | 5.7 | Negligible |

Table 2
Product distribution (wt %) at various reaction conditions for the *1,2,4-Trimethylbenzene* transformation reactions

| Temp (°C)/ time (s) | Conv. (%) | Gas | Benzene | <i>1,3,5</i> - TMB | <i>1,2,3</i> - TMB | TI * | <i>p</i> - xylene | <i>m</i> - xylene | <i>o</i> - xylene | Toluene | TeMB's (<i>1,2,3,4</i> - <i>1,2,3,5</i> - & <i>1,2,4,5</i>) | TD * |
|------------------------|-----------|-----|---------|-----------------------|-----------------------|-------------|----------------------|----------------------|----------------------|---------|--|-------------|
| 400 | | | | | | | | | | | | |
| 5 | 12.6 | - | - | 2.0 | 1.0 | 3.0 | 0.9 | 2.1 | 1.3 | 0.5 | 3.7 | 8.0 |
| 10 | 23.0 | 0.1 | - | 3.8 | 1.8 | 5.6 | 1.7 | 4.0 | 2.5 | 0.8 | 8.0 | 16.2 |
| 15 | 31.3 | 0.1 | 0.0 | 5.2 | 2.5 | 7.7 | 2.3 | 5.5 | 3.4 | 1.2 | 11.6 | 22.7 |
| 450 | | | | | | | | | | | | |
| 5 | 15.6 | 0.1 | - | 2.6 | 1.3 | 3.9 | 1.1 | 2.5 | 1.5 | 0.6 | 4.8 | 9.8 |
| 10 | 26.9 | 0.1 | - | 4.4 | 2.1 | 6.6 | 1.9 | 4.3 | 2.6 | 1.0 | 9.0 | 17.8 |
| 15 | 36.0 | 0.2 | 0.1 | 6.0 | 2.8 | 8.8 | 2.5 | 5.8 | 3.4 | 1.4 | 12.2 | 23.8 |
| 500 | | | | | | | | | | | | |
| 5 | 16.2 | 0.2 | - | 2.7 | 1.3 | 4.1 | 1.1 | 2.6 | 1.5 | 0.7 | 4.9 | 10.1 |
| 10 | 28.2 | 0.3 | 0.1 | 4.7 | 2.3 | 7.0 | 2.0 | 4.5 | 2.6 | 1.2 | 9.1 | 18.1 |
| 15 | 38.0 | 0.5 | 0.1 | 6.2 | 2.9 | 9.1 | 2.7 | 6.3 | 3.5 | 1.7 | 11.8 | 24.3 |

*TI – Total isomerization

**TD – Total Disproportionation

Table 3
Product distribution (wt %) at various reaction conditions for 1,3,5-Trimethylbenzene transformation reactions

| Temp (°C)/ time (s) | Conv. (%) | Gas | Benzene | 1,2,4-TMB | 1,2,3-TMB | TI* | p-xylene | m-xylene | o-xylene | Toluene | TeMB's (1,2,3,4-, 1,2,3,5-, & 1,2,4,5) | TD** |
|------------------------|-----------|-------|---------|-----------|-----------|-------|----------|----------|----------|---------|--|-------|
| 400 | | | | | | | | | | | | |
| 3 | 6.97 | - | - | 2.67 | 0.30 | 2.97 | 0.30 | 1.32 | 0.39 | 0.21 | 1.45 | 3.46 |
| 5 | 13.01 | - | - | 5.03 | 0.60 | 5.63 | 0.57 | 2.32 | 0.76 | 0.35 | 3.04 | 6.69 |
| 7 | 17.25 | - | - | 6.47 | 0.79 | 7.26 | 0.70 | 3.16 | 0.96 | 0.42 | 4.23 | 9.05 |
| 10 | 23.71 | - | - | 8.93 | 1.11 | 10.04 | 0.97 | 4.20 | 1.32 | 0.55 | 6.03 | 12.52 |
| 13 | 31.76 | - | - | 11.85 | 1.51 | 13.36 | 1.32 | 5.33 | 1.76 | 0.74 | 8.41 | 16.82 |
| 15 | 34.89 | - | - | 13.43 | 1.67 | 15.10 | 1.43 | 5.68 | 1.95 | 0.75 | 9.10 | 18.16 |
| 450 | | | | | | | | | | | | |
| 3 | 8.93 | - | - | 3.50 | 0.41 | 3.91 | 0.42 | 1.45 | 0.54 | 0.28 | 1.95 | 4.36 |
| 5 | 16.27 | - | - | 6.41 | 0.79 | 7.20 | 0.75 | 2.56 | 0.97 | 0.44 | 3.85 | 8.13 |
| 7 | 20.86 | - | - | 8.06 | 1.03 | 9.09 | 0.94 | 3.28 | 1.23 | 0.55 | 5.15 | 10.60 |
| 10 | 29.74 | 0.086 | - | 11.12 | 1.50 | 12.62 | 1.37 | 4.27 | 1.72 | 0.79 | 7.94 | 15.30 |
| 13 | 35.19 | 0.079 | - | 13.29 | 1.76 | 15.05 | 1.58 | 5.38 | 2.04 | 0.89 | 9.22 | 18.22 |
| 15 | 40.33 | 0.104 | - | 15.32 | 2.05 | 17.37 | 1.86 | 5.90 | 2.38 | 1.04 | 10.60 | 20.74 |
| 500 | | | | | | | | | | | | |
| 3 | 10.53 | - | - | 4.17 | 0.55 | 4.72 | 0.54 | 1.47 | 0.66 | 0.35 | 2.38 | 5.05 |
| 5 | 18.47 | 0.103 | - | 6.95 | 0.99 | 7.94 | 0.97 | 2.57 | 1.17 | 0.62 | 4.49 | 9.20 |
| 7 | 24.83 | 0.141 | - | 9.38 | 1.37 | 10.75 | 1.28 | 3.36 | 1.57 | 0.79 | 6.18 | 12.39 |
| 10 | 32.01 | 0.226 | - | 11.88 | 1.75 | 13.63 | 1.66 | 4.44 | 2.02 | 1.05 | 8.06 | 16.18 |
| 13 | 39.45 | 0.254 | - | 14.81 | 2.18 | 16.99 | 2.02 | 5.31 | 2.47 | 1.23 | 10.11 | 19.91 |
| 15 | 43.92 | 0.354 | - | 16.29 | 2.39 | 18.68 | 2.27 | 6.00 | 2.75 | 1.41 | 11.27 | 22.29 |

*TI – Total isomerization

**TD – Total Disproportionation

Table 4
Estimated Kinetic Parameters Based on Time on Stream (TOS Model) – 1,3,5-TMB

| Parameters | Values | |
|---|----------|------------|
| | k_{so} | k_{disp} |
| E_i (kJ/mol) | 14.22 | 15.64 |
| 95% CL | 2.92 | 3.17 |
| $k_{oi}^a \times 10^3$ (m ³ /kg of catalyst.s) | 0.90 | 0.03 |
| 95% CL $\times 10^3$ | 0.05 | 0.001 |
| $\alpha = 0.001$ (95% CL of 0.008) | | |

^apre-exponential factor as obtained from equation (7); unit for second order (m⁶/kg of catalyst.s)

Table 5
Correlation Matrix for Parameters – 1,3,5-TMB

| | k_{0iso} | E_{iso} | k_{0disp} | E_{disp} | α |
|-------------|------------|-----------|-------------|------------|----------|
| k_{0iso} | 1.0000 | 0.0917 | 0.5845 | 0.0190 | 0.8682 |
| E_{iso} | -0.0917 | 1.0000 | 0.0397 | 0.4605 | -0.0130 |
| k_{0disp} | 0.5845 | 0.0397 | 1.0000 | -0.0867 | 0.8225 |
| E_{disp} | 0.0190 | 0.4605 | -0.0867 | 1.0000 | -0.0287 |
| α | 0.8682 | -0.0130 | 0.8225 | -0.0287 | 1.0000 |

Table 6
Estimated Kinetic Parameters Based on Time on Stream (TOS Model) – 1,2,4-TMB

| Parameters | Values | |
|---|----------|------------|
| | k_{so} | k_{disp} |
| E_i (kJ/mol) | 14.31 | 10.07 |
| 95% CL | 3.17 | 1.49 |
| $k_{0i}^a \times 10^3$ (m ³ /kg of catalyst.s) | 0.47 | 0.03 |
| 95% CL $\times 10^3$ | 0.02 | 0.001 |
| $\alpha = 0.013(95\% \text{ CL of } 0.005)$ | | |

^apre-exponential factor as obtained from equation (7); unit for second order (m⁶/kg of catalyst.s)

Table 7
Correlation Matrix for Parameters – 1,2,4-TMB

| | k_{0iso} | E_{iso} | k_{0disp} | E_{disp} | α |
|-------------|------------|-----------|-------------|------------|----------|
| k_{0iso} | 1.0000 | 0.1262 | 0.4909 | 0.0330 | 0.7186 |
| E_{iso} | -0.1261 | 1.0000 | 0.0272 | 0.4910 | -0.0046 |
| k_{0disp} | 0.4909 | 0.0272 | 1.0000 | -0.0418 | 0.8948 |
| E_{disp} | 0.0330 | -0.4910 | -0.0418 | 1.0000 | -0.0223 |
| α | 0.7186 | -0.0046 | 0.8948 | -0.0223 | 1.0000 |

Figure Captions

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- Fig. 1: 1,3,5-Triethylbenzene conversion with reaction time and temperature
- Fig. 2: Xylene yields versus 1,3,5-TMB conversion
- Fig. 3: Isomerization yield versus conversion at several temperatures
- Fig. 4: TeMB yield versus conversion for both catalysts
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- Fig. 8: P/O ratio versus conversion for 1,3,5-TMB (\square) and 1,2,4-TMB (\blacklozenge) at **a)** 400°C; **b)** 500°C
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- Fig. 13: D/I ratio versus conversion for 1,3,5-TMB (\square) and 1,2,4-TMB (\blacklozenge) at **a)** 400°C; **b)** 500°C

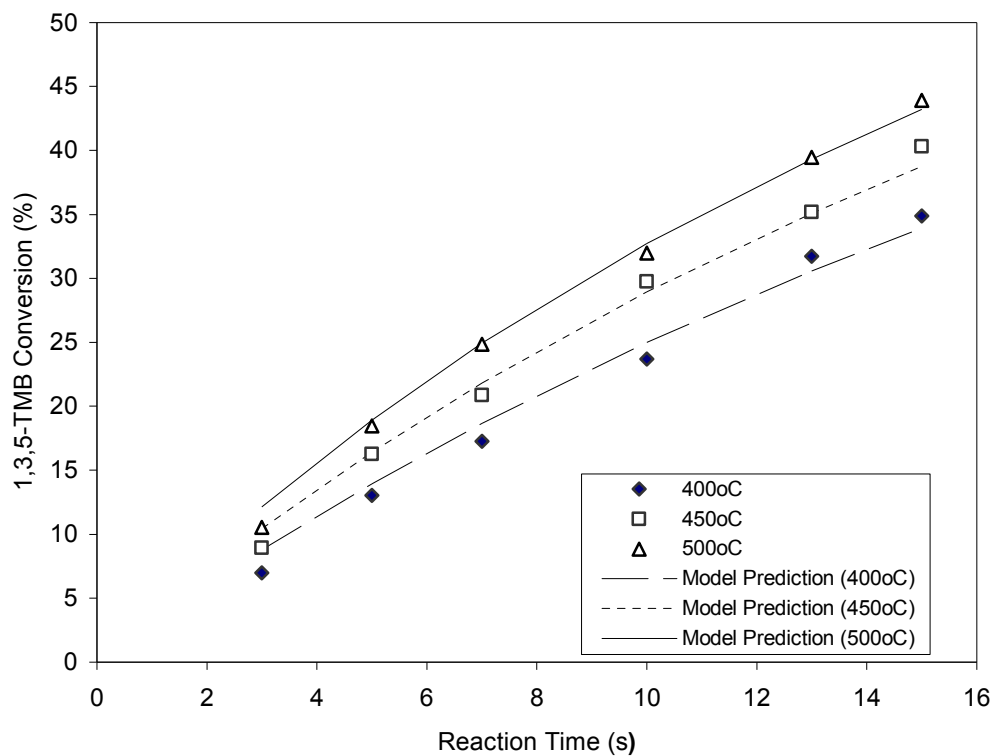


Fig. 1. 1,3,5-Trimethylbenzene conversion with reaction time and temperature

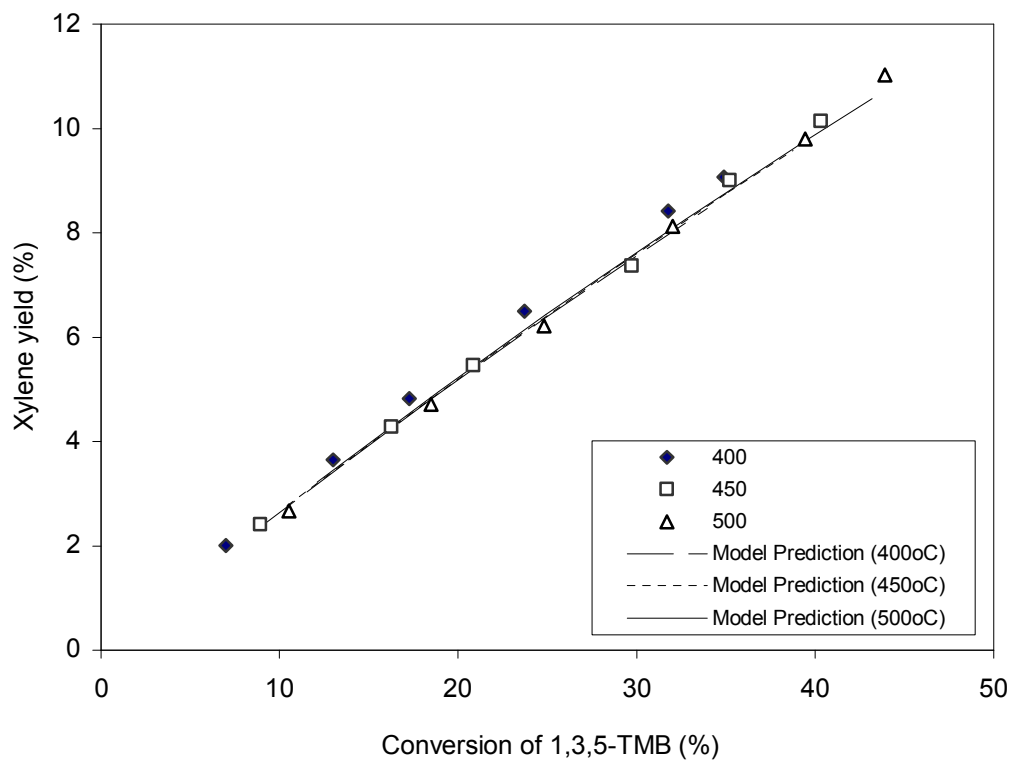


Fig. 2. Xylene yields versus 1,3,5-TMB conversion

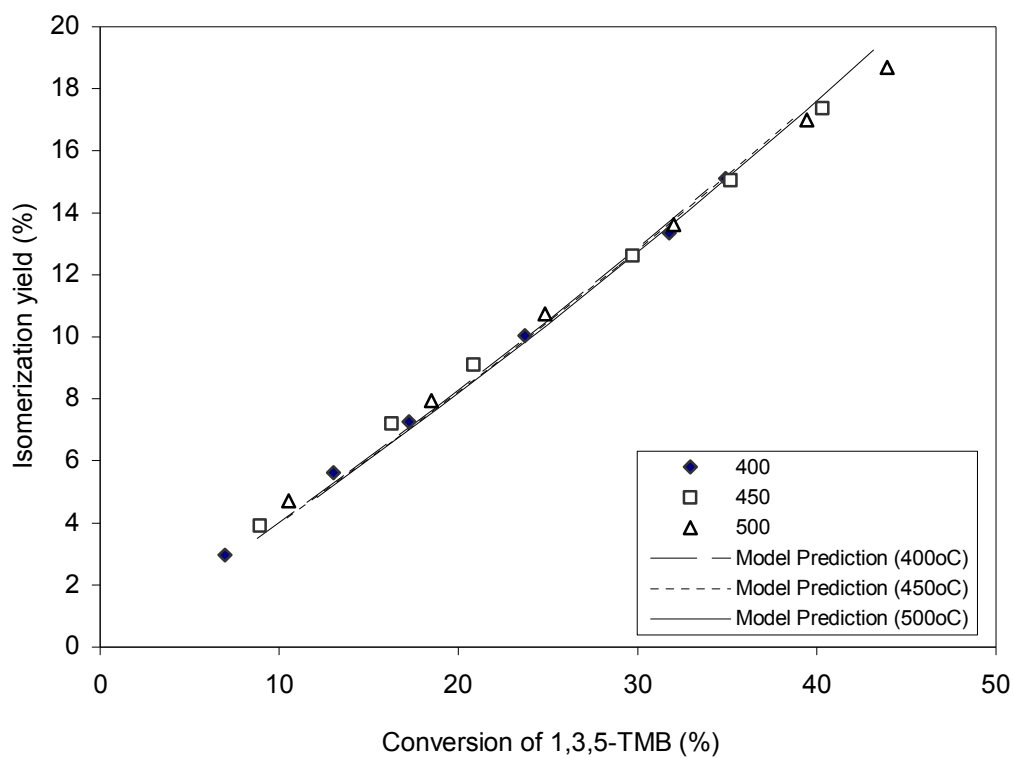


Fig. 3. Isomerization yield versus conversion at several temperatures

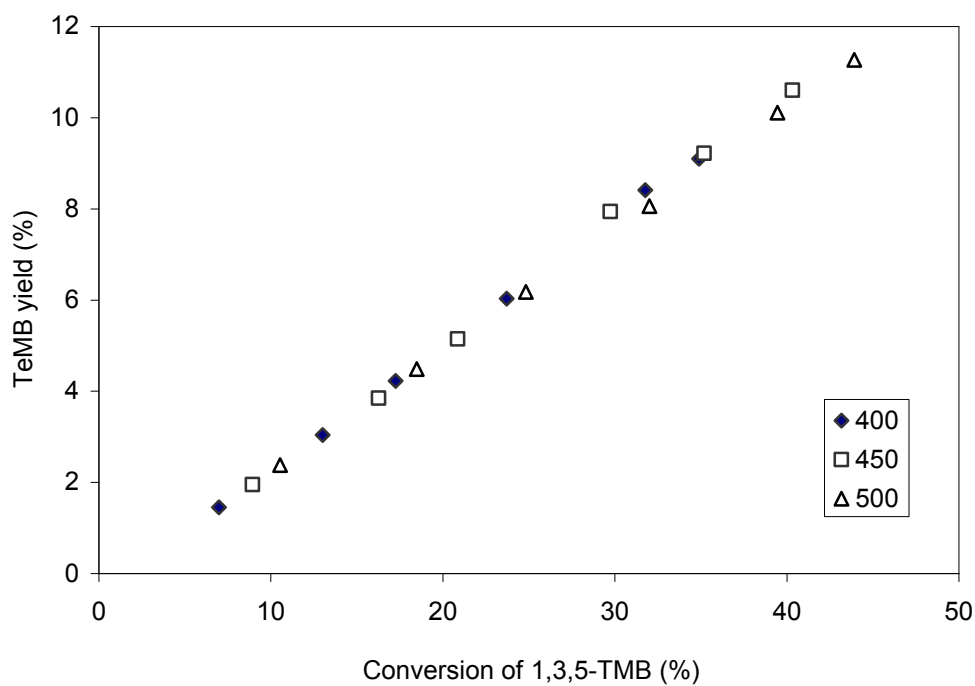


Fig. 4. TeMB yield versus 1,3,5-TMB conversion

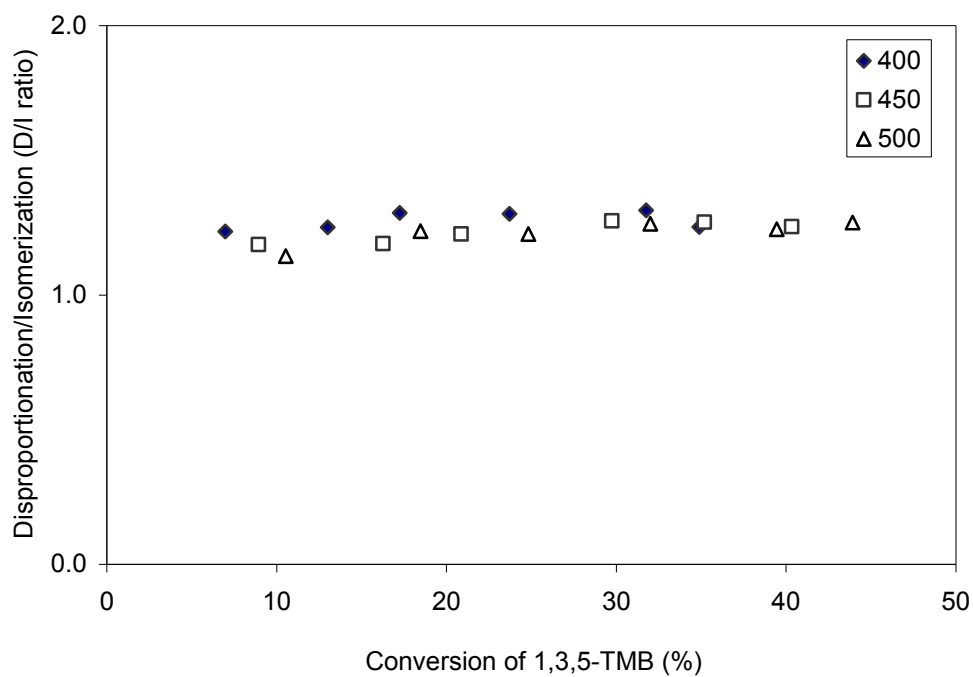
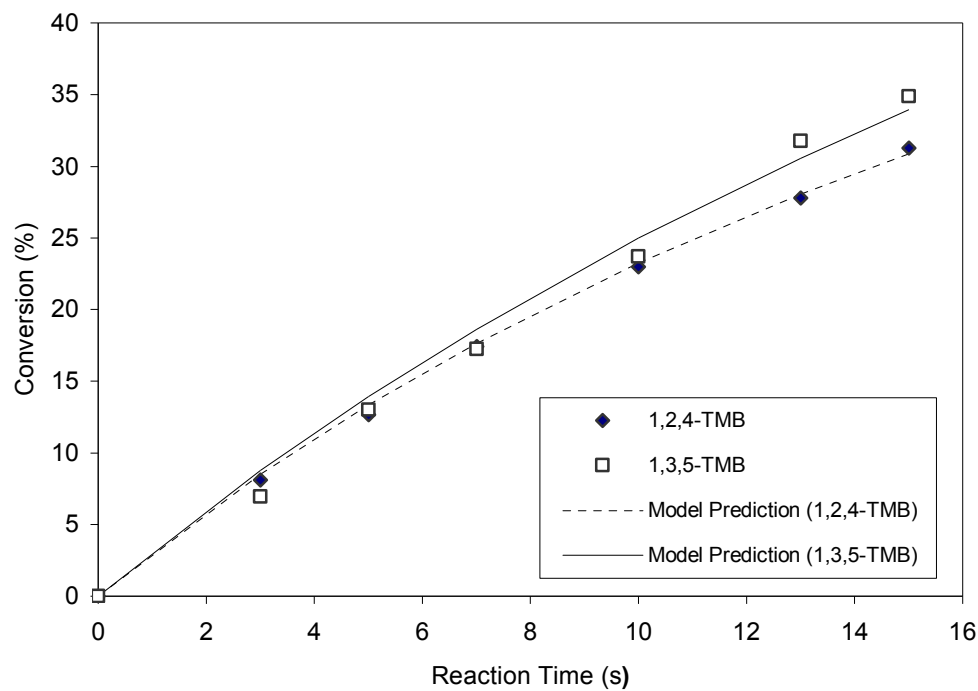


Fig. 5. D/I ratio versus 1,3,5-TMB conversion

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b.

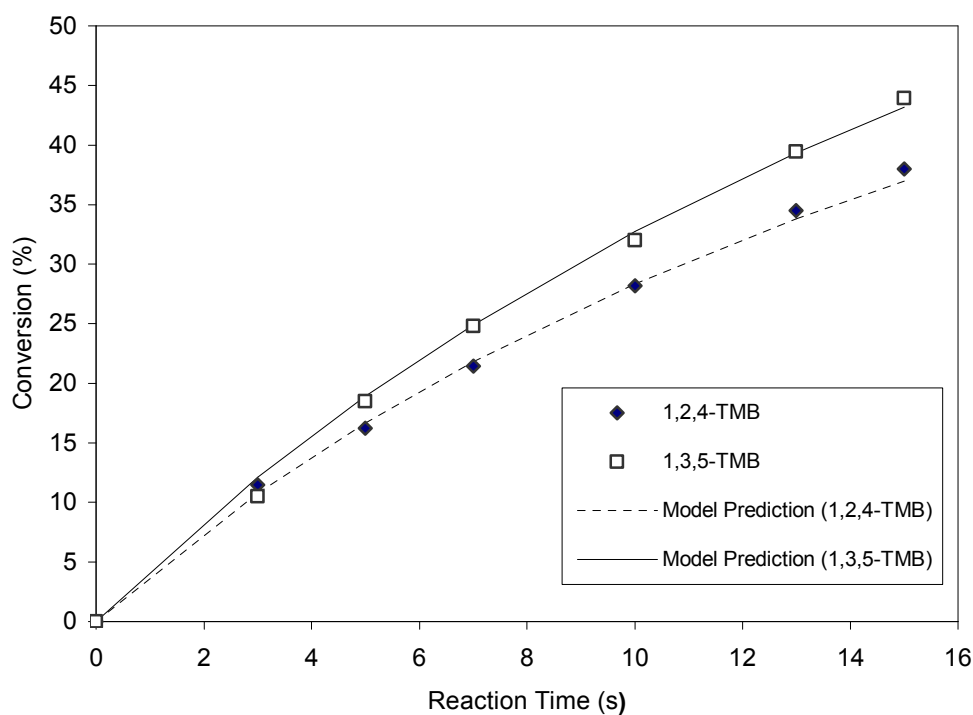
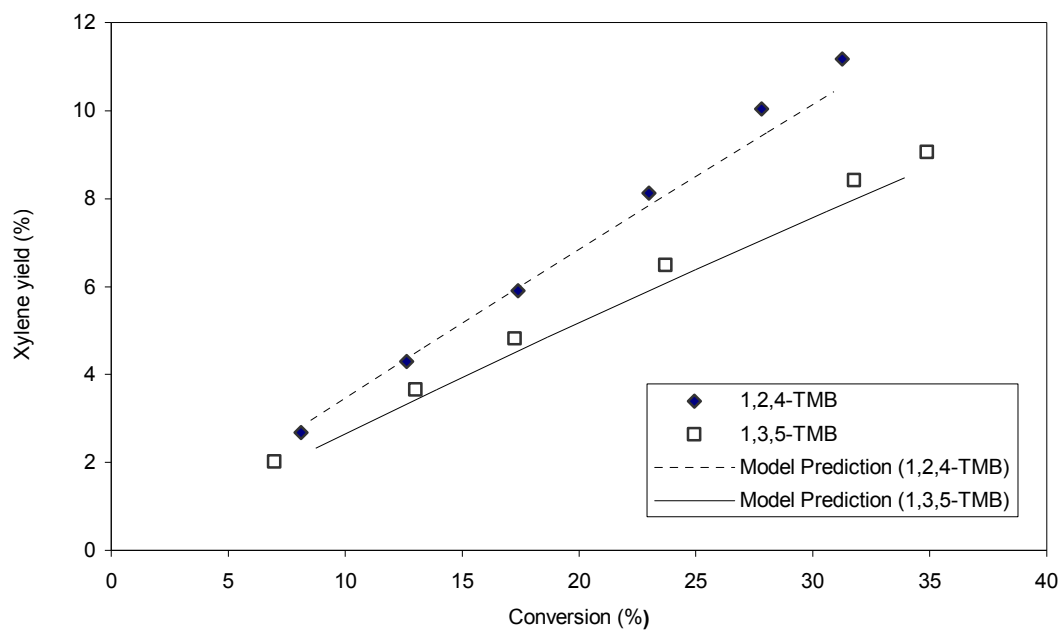


Fig. 6. Reactivity comparisons between 1,3,5-TMB (\square) and 1,2,4-TMB (\blacklozenge) at **a)** 400°C; **b)** 500°C

a.



b.

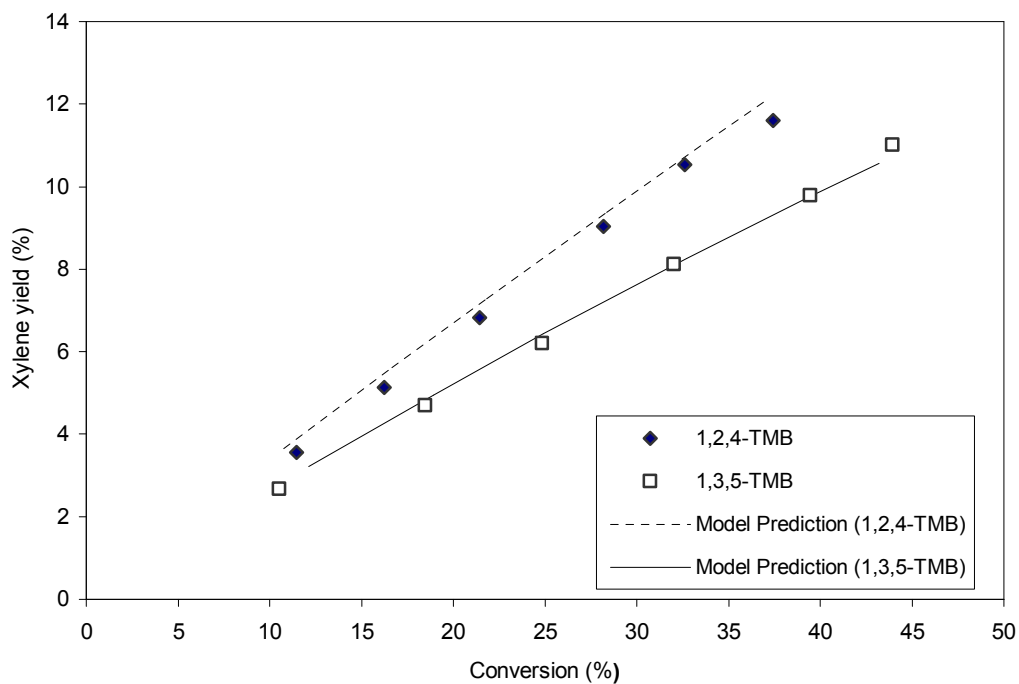


Fig. 7. Xylene yield versus conversion for 1,3,5-TMB (\square) and 1,2,4-TMB (\blacklozenge) at **a)** 400°C; **b)** 500°C

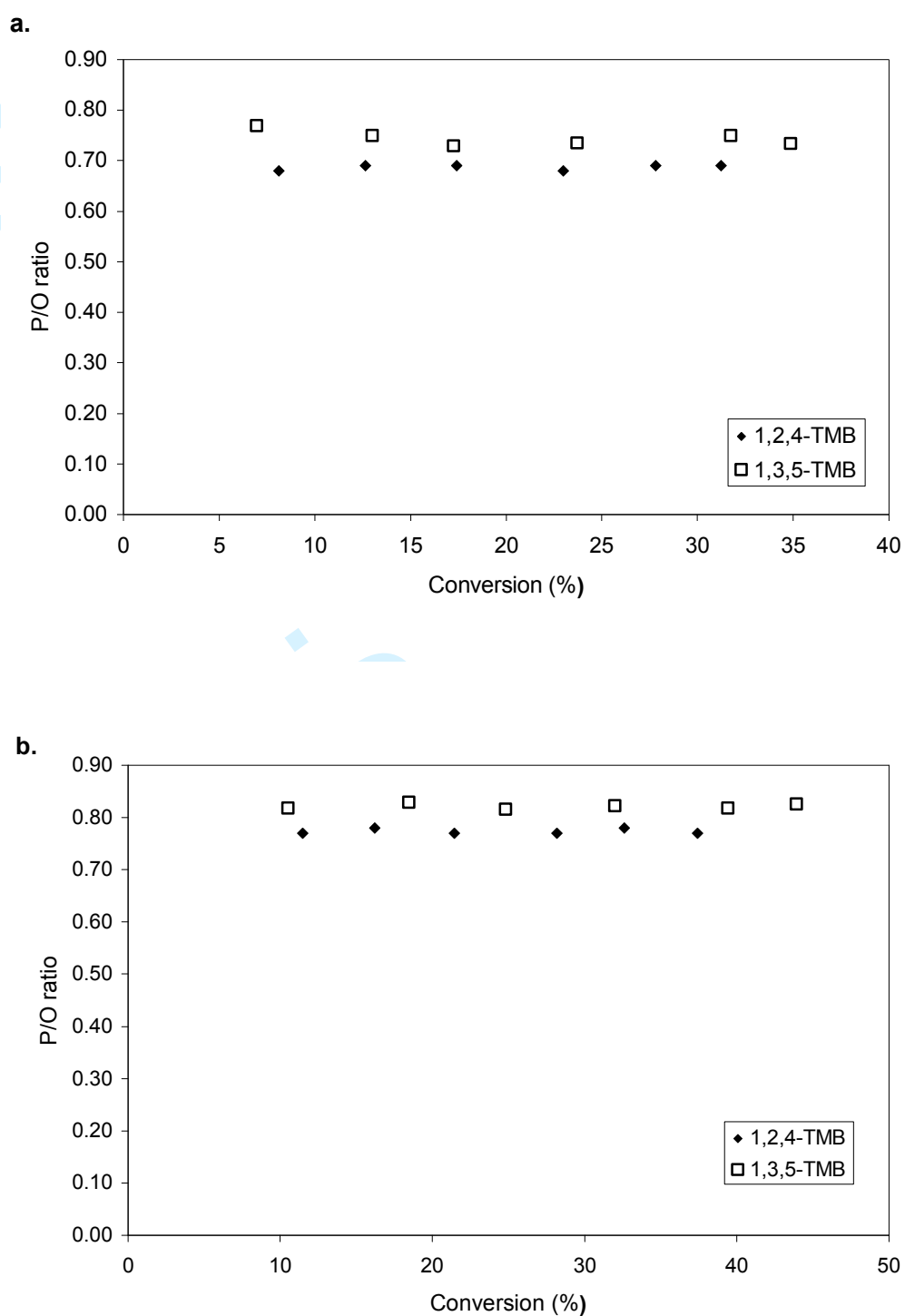


Fig. 8. P/O ratio versus conversion for 1,3,5-TMB (\square) and 1,2,4-TMB (\blacklozenge) at **a)** 400°C; **b)** 500°C

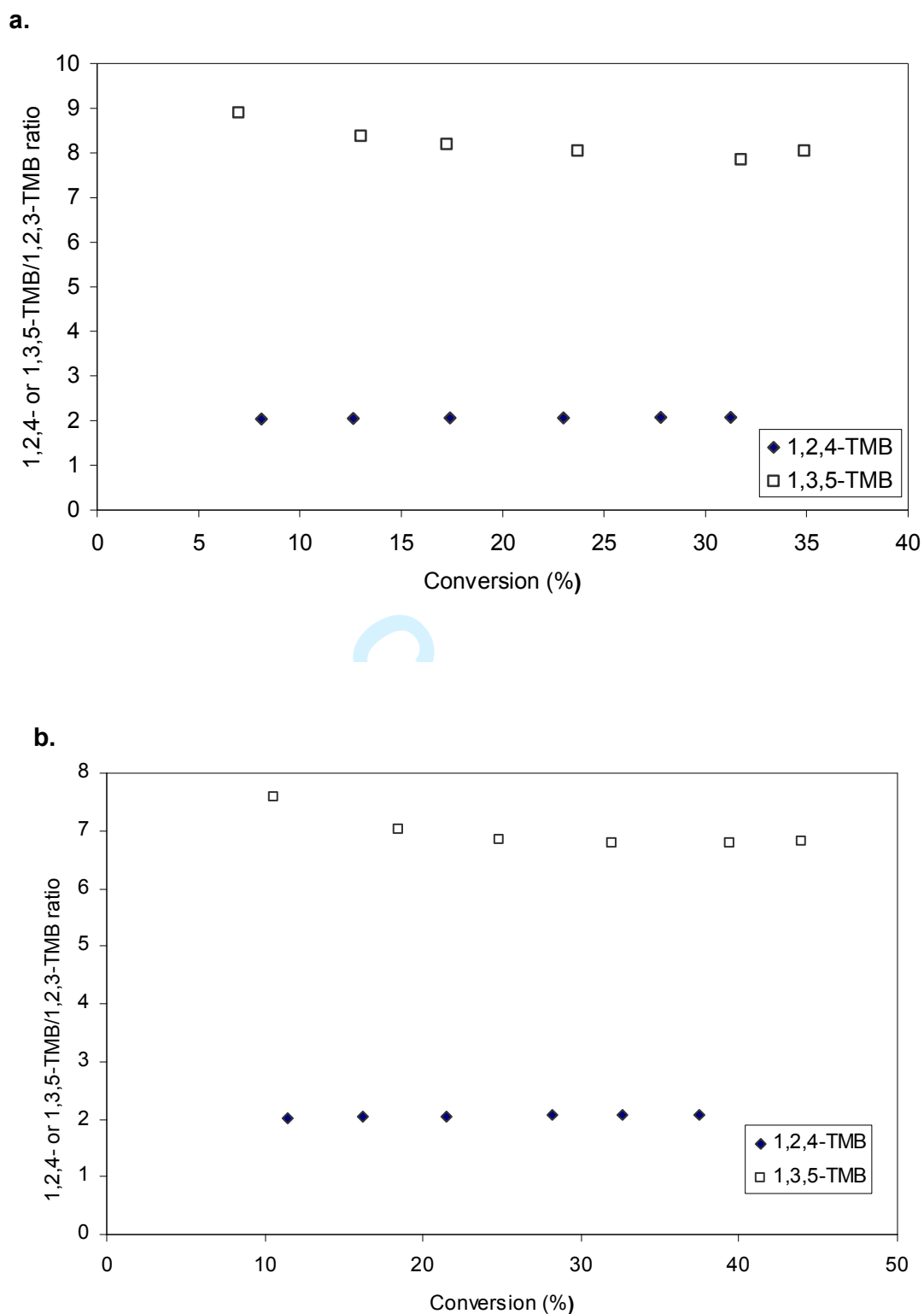


Fig. 9: Distribution of TMB isomers versus conversion for 1,3,5-TMB (\square) and 1,2,4-TMB (\blacklozenge) at **a)** 400°C; **b)** 500°C

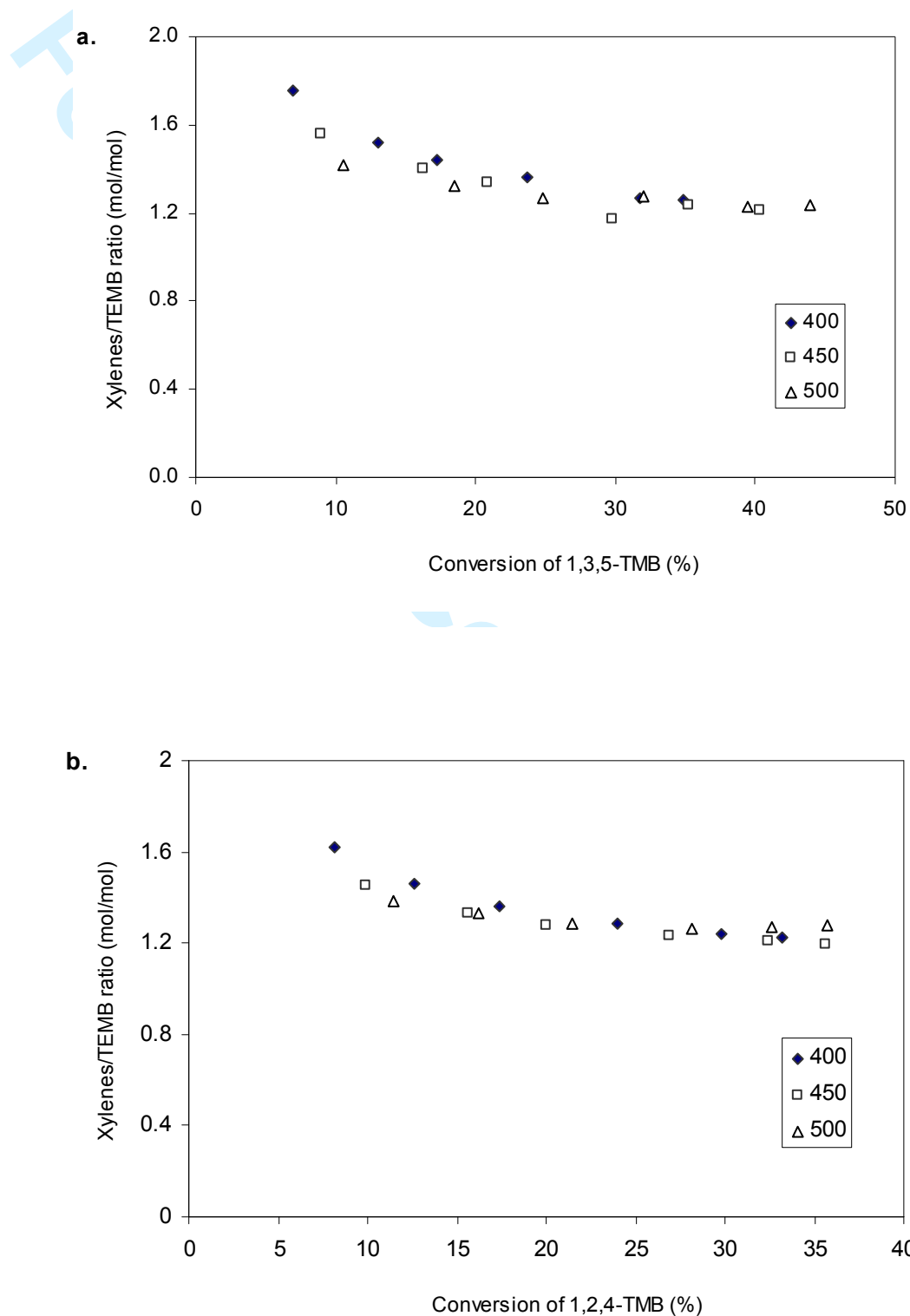


Fig. 10. Xylenes/TeMBs molar ratio versus conversion at several temperatures for **a)** 1,3,5-TMB and **b)** 1,2,4-TMB (◆)

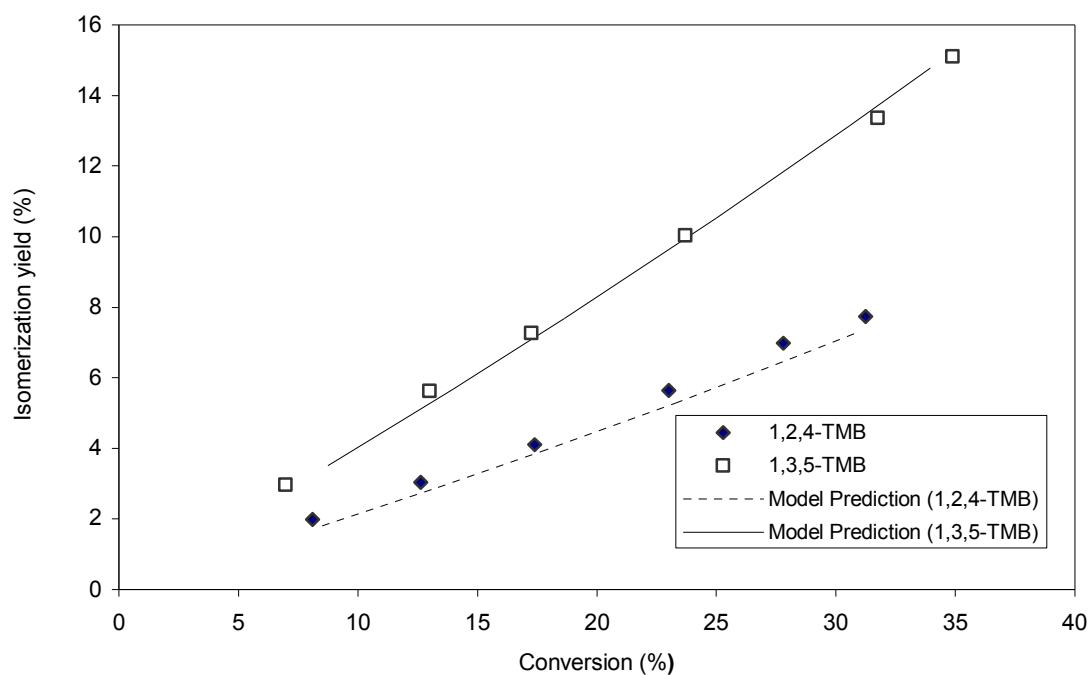


Fig. 11. Isomerization yield versus conversion for 1,3,5-TMB (\square) and 1,2,4-TMB (\blacklozenge) at 400°C

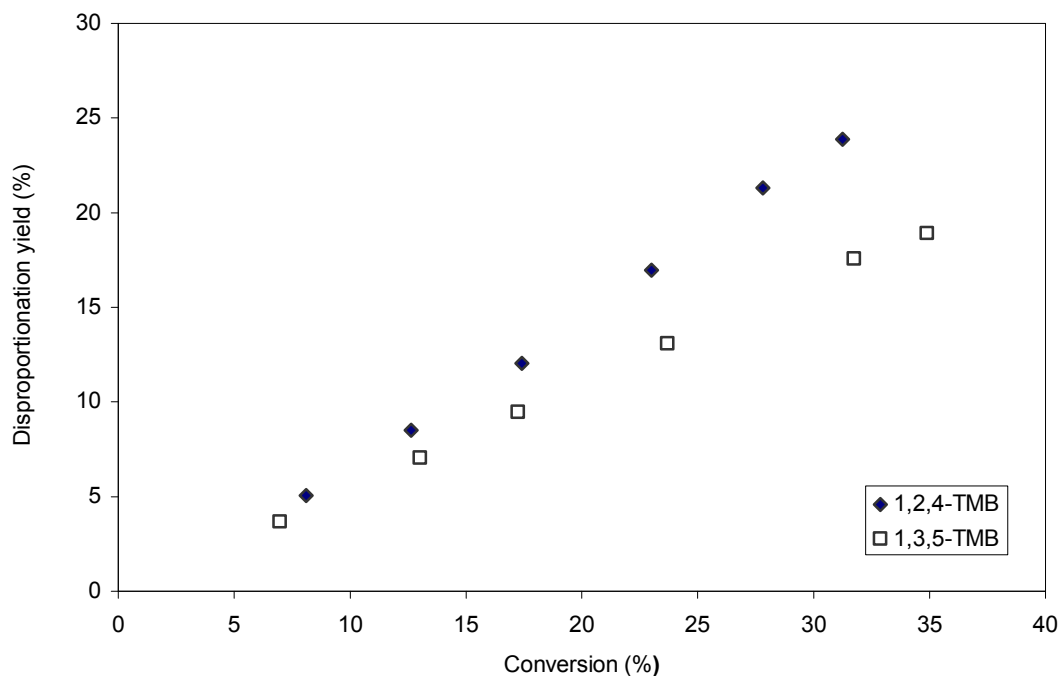


Fig. 12. Disproportionation yield versus conversion for 1,3,5-TMB (\square) and 1,2,4-TMB (\blacklozenge) at 400°C

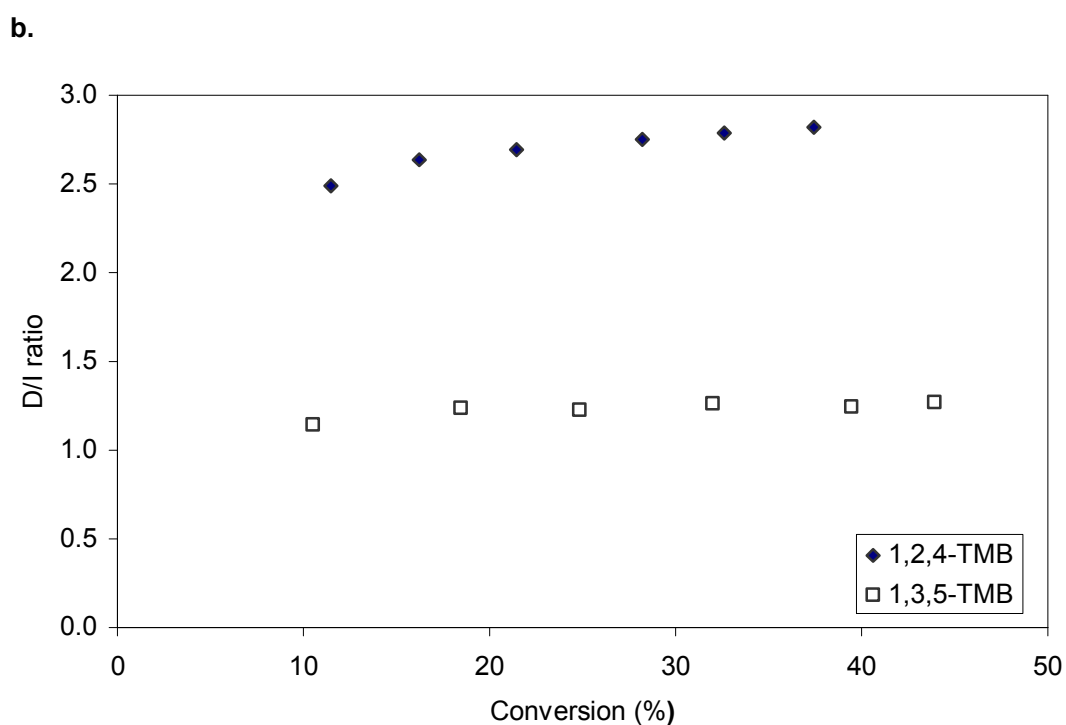
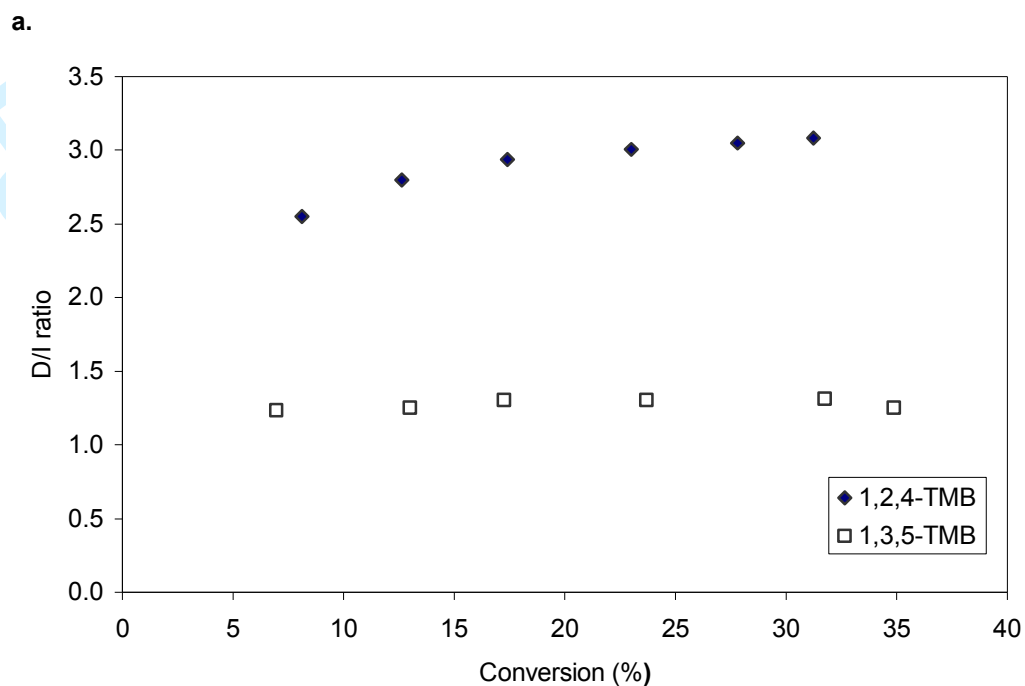


Fig. 13. D/I ratio versus conversion for 1,3,5-TMB (\square) and 1,2,4-TMB (\blacklozenge) at **a)** 400°C; **b)** 500°C