

# Catalytic Transformation of C<sub>7</sub>-C<sub>9</sub> Methyl Benzenes over USY and ZSM-5 based FCC Zeolite Catalysts

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## Abstract

Catalytic transformation of three methyl benzenes (*toluene*, *m-xylene*, and *1,2,4-trimethyl benzene*) has been investigated over two FCC zeolite catalysts in a novel riser simulator at different operating conditions. The two catalysts are based on Y-zeolite (FCC-Y) and ZSM-5 (FCC-Z). The effect of reaction conditions on the variation of isomerization to disproportionation products ratio (I/D), distribution of trimethylbenzene (TMB) isomers (1,3,5-to-1,2,3-) and values of *p*-xylene/*o*-xylene (P/O) ratios are reported. The sequence of reactivity of the three alkyl benzenes was found to decrease as the number of methyl group per benzene ring decreases, as follows: *1,2,4-trimethyl benzene* > *m-xylene* > *toluene*. This is true at all temperatures over the FCC-Y zeolite catalyst. It is also true over the FCC-Z for low to moderate temperatures. However at 500°C, the reactivity of *m-xylene* was found to be comparable to that of 1,2,4-TMB. Furthermore, The FCC-Y consistently showed higher conversions for the 1,2,4-TMB than FCC-Z despite the fact that the acidity of the FCC-Z catalyst is almost 7 times higher than that of the FCC-Y. However, for the *m-xylene* transformation, FCC-Z showed higher activity than the FCC-Y. This phenomenon is explained by the complex inter-relationship between acidity and the zeolite system architecture, as well as competition between reaction and diffusion during the transformation reactions.

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*Keywords:* FCC zeolite catalysts; ZSM-5; USY; Toluene; *m*-Xylene; Disproportionation; Isomerization

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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 to increase xylene production processes. In the year 1999, the world consumption of mixed xylene was about 24 million tons, and is expected to grow at a rate of 6.2% to 32.5 million tons by the year 2004. This indicates that xylenes are still gaining importance in the petrochemical market. Most of the currently working isomerization plants are using zeolite based catalysts.

One common way for xylene production is the conversion of the lower value toluene (C<sub>7</sub>) and trimethylbenzene (C<sub>9</sub>) into xylenes. Huge research has been devoted for this purpose. It is well known that these hydrocarbons undergo several simultaneous chemical reactions which include; Isomerization, disproportionation, transalkylation, dealkylation, and coke formation.

Toluene transformation is well documented in the literature [1,2,3]. Two toluene molecules react together to form benzene and xylene. Most of the reported studies on toluene disproportionation have been conducted in relatively high pressure and in the presence of hydrogen using fixed bed reactor. The equilibrium mixture contains approximately 24% *p*-xylene, 54% *m*-xylene and 22% *o*-xylene in the temperature range of 250-450°C. ZSM-5 zeolites can be used in toluene disproportionation to enhance *para*-selectivity higher than 90% [4].

Detailed mechanism of toluene disproportionation over ZSM-5 zeolite was reported by Xiong et al.[1]. Two different reaction pathways were proposed, i.e., methyl transfer mechanism (formation of a methoxy group on the zeolite surface) and the diphenyl methane mechanism. It was shown that toluene disproportionation does not require Brønsted acid sites of a high acid strength (present in H-ZSM-5 zeolite) to proceed, and the rate of the reaction is controlled by the concentration of acid sites, which is higher in zeolite Y compared to H-ZSM-5 [1]. Other researchers have studied toluene disproportionation using ion-exchanged HZSM-5 with Ni, Cr, Mg, Bi and Zn [5].

*m*-xylene isomerizes to the *para* and *ortho* isomers and can disproportionate into trimethylbenzenes (TMBs) and toluene. Catalytic data of *m*-xylene transformation over acid catalysts provides insights into catalyst structure and pore-size [6]. Larger value of the *para/ortho* (P/O) ratio of the products corresponds to smaller catalyst pore size and vice versa. The distribution of trimethylbenzenes gives useful information about the pore

structure of zeolites [7]. In zeolites with 12 MR, Martens et al. [8] showed that zeolites with adjacent cages favor the formation of the bulky 1,3,5-trimethylbenzene isomer while zeolites with straight channels and side pockets at regular distances, such as mordenite (MOR), are favorable for the formation of the 1,2,3-trimethylbenzene isomer. The ratio of the rates of isomerization to disproportionation (I/D), similar to the P/O ratio, is useful in providing information about the pore or cage size. Since disproportionation necessarily requires a bimolecular reaction, larger pore systems that can accommodate the required transition state give more disproportionation. In addition, the *m*-xylene reactions can also provide a means of determining rates of deactivation via carbon depositing mechanisms [9].

Ilyas and Al-Khattaf [10] have carried out a systematic study on the influence of reaction conditions (temperature, time, and reactant type) on the selectivity of xylene transformation 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. Furthermore, a comprehensive kinetic model for xylenes isomerization and disproportionation has been reported by Ilyas and Al-Khattaf [11] and Al-Khattaf et al., [12]. This kinetic modeling is based on the triangular reaction scheme and time on stream deactivation function. All activation energies for different reaction steps have been evaluated and compared with literature.

Shape selective conversion of xylenes over ZSM-5 has been investigated in detail by several workers [13]. The interest directed on ZSM-5 is a result of its high activity and shape selectivity. ZSM-5 zeolite presents very strong shape selectivity as a result of their geometry and architecture of their channel systems. Being a medium-pore size zeolite, *reactant shape selectivity* (which restricts or promotes transportation of reactant molecule into the zeolite channels) and *restricted transition state shape selectivity* (which prevents the formation of bulky reaction intermediates) play very significant roles in its reactions. Modification of ZSM-5 by various compounds has been employed to enhance *p*-xylene

selectivity from xylene isomerization process. Similarly, *para*-selectivity was improved by the selective coking of the external surface of ZSM-5 [14-16].

Trimethyl benzene 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. [17] 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 amount of xylene and tetramethylbenzene (TeMBs) isomers. 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. They also observed that the pre-dried LaY catalyst was 2 to 3 times more active for disproportionation than the other catalyst calcined by rapid heating of the wet cake. They also found that all three xylene isomers were produced from the disproportionation of 1,2,4-TMB. However, at lower conversions, *ortho*- was formed in preference to *para*- xylene due to the fact that removal of 2-methyl group to form *para*- is more difficult than the removal of the methyl group from either 1<sup>st</sup> or 4<sup>th</sup> position of 1,2,4-TMB. Both 1,3,5- and 1,2,3-TMB isomers were the products of the isomerization of 1,2,4-TMB. Due to the ortho-para directing effect of methyl groups, 1,2,4-TMB produced all three isomers of TeMB.

Roger et al. [18,19] studied the conversion of 1,2,4- Trimethylbenzene (1,2,4-TMB) over amorphous silica-alumina and HZSM5 in the gas phase and investigated the effect of pore mouth narrowing. They concluded that paring reaction played a decisive role during the conversion over HZSM5 at elevated temperature (450°C) and in the reaction sequence, xylenes and tetramethylbenzenes (TeMBs) were intermediates. Over both silica-alumina and HZSM5, isomerization of 1,2,4-TMB to 1,2,3- and 1,3,5-TMB isomers were found to be the most rapid reaction with about 90% selectivity at low conversion and this 1,2-methyl-shift were shown to take place on the external surface of the zeolite crystals. They also reported that over silica-alumina, the reaction almost terminated at the disproportionation step, whereas over HZSM5, 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.

Recently, Atias et al. [20] developed a heterogeneous kinetic model for the catalytic conversion of 1,2,4-trimethylbenzene in a CREC riser using USY zeolite catalysts under FCC operating conditions. They determined the intrinsic kinetic parameters for both isomerization and disproportionation reactions. Cejka et al. [21] studied the effect of the structure of large pore zeolites on the activity, selectivity and time-on-stream (T-O-S) in trimethyl benzene disproportionation. They used zeolites of beta, Y, L and Mordenite types which exhibited significant difference in conversion and T-O-S. They found higher conversions of TMBs and high selectivity to xylenes and TMBs at 400°C with zeolites Y and beta (which provides optimum reaction space) compared to other large pore sieves (Mordenite and zeolites L). They also measured the diffusion coefficients of 1,2,4- and 1,3,5-TMBs and 1,2,3,5-TeMBs at 25 and 100°C over zeolites Y, beta/1 and Mordenite and the measured values followed the decreasing order of *m*-xylene >> 1,2,4-TMB > 1,3,5-TMB ≈ TeMB.

Although abundant literature has been published on alkyl benzenes transformation, however, in most instances, fixed-bed reactor was utilized for the reaction. Thus, the present study is aimed at investigating alkyl benzenes transformation (toluene, *m*-xylene, and 1,2,4-trimethyl benzene) over two FCC zeolite catalysts in a fluidized-bed reactor. The study will focus on the effect of catalyst structure and reaction conditions (time, temperature, and conversion) on the variation of the ratios of disproportionation to isomerization products (D/I), distribution of trimethylbenzene (TMB) isomers (1,3,5-to-1,2,3-) and values of *p*-xylene/*o*-xylene (P/O) ratios .

## **2. Experimental Procedure**

### **2.1 The Riser Simulator**

All the experimental runs were carried out in the Riser Simulator. This reactor is a novel bench scale equipment with internal recycle unit invented by de Lasa [22] to overcome the technical problems of the standard micro-activity test (MAT), and it is fast becoming a valuable experimental tool for reaction evaluation involving model compounds [23,24], and also for testing and developing new FCC in VGO cracking [25,26]. The Riser Simulator consists of two outer shells, the lower section and the upper section which allow to load or to unload the catalyst easily. The reactor was designed in such way that an annular space is created between the outer portion of the basket and the inner part of the

reactor shell. A metallic gasket seals the two chambers with an impeller located in the upper section. A packing gland assembly and a cooling jacket surrounding the shaft provide support for the impeller. Upon rotation of the shaft, gas is forced outward from the center of the impeller towards the walls. This creates a lower pressure in the centre region of the impeller thus inducing flow of gas upward through the catalyst chamber from the bottom of the reactor annular region where the pressure is slightly higher. The impeller provides a fluidized bed of catalyst particles as well as intense gas mixing inside the reactor. A schematic diagram of the Riser Simulator is shown in **Fig. 1**. A detailed description of various Riser Simulator components, sequence of injection and sampling can be found in Kraemer [27].

## 2.2 Materials

Ultrastable Y zeolite (USY) was obtained from Tosoh Company. The Na-zeolite was ion exchanged with  $\text{NH}_4\text{NO}_3$  to replace the sodium cation with  $\text{NH}_4^+$ . Following this,  $\text{NH}_3$  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- $\mu\text{m}$  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 during 2 hr at 600°C. Finally, the fluidizable catalyst particles (60- $\mu\text{m}$  average size) were treated with 100% steam at 760°C for 5 hr (FCC-Y). The ZSM-5 zeolite (FCC-Z) used in this work was ion exchanged with  $\text{NH}_4\text{NO}_3$  to replace the Na cation with  $\text{NH}_4^+$ . Following this,  $\text{NH}_3$  was removed and the H form of the zeolite was spray-dried using kaolin as the filler and a silica sol as the binder. The resulting 60  $\mu\text{m}$  catalyst particles had the following composition: 30 wt % zeolite, 50 wt % kaolin, and 20 wt % silica. The process of Na removal was repeated for the pelletized catalyst. Following this, the catalyst was calcined at 600°C for 2 h. Table 1 reports the catalyst main properties following catalyst pre-treatment. The unit cell size was determined by X-ray diffraction following ASTM D-3942-80. Surface area was measured using the BET method.

Analytical grade (99% purity) pure toluene, *m*-xylene, and 1,2,4-trimethylbenzene were obtained from Sigma-Aldrich. All chemicals were used as received as no attempt was made to further purify the samples.

### **2.3 Procedure**

Regarding the experimental procedure in the Riser Simulator, 0.8g of catalyst was weighed and loaded into the Riser Simulator basket. The system was then sealed and tested for any pressure leaks by monitoring the pressure changes in the system. Furthermore, the reactor was heated to the desired reaction temperature. The vacuum box was also heated to around 250°C and evacuated at around 0.5psi to prevent any condensation of hydrocarbons inside the box. The heating of the Riser Simulator was conducted under continuous flow of inert gases (argon) and the process usually takes few hours until thermal equilibrium is finally attained. Meanwhile, before the initial experimental run, the catalyst was activated for 15 minutes at 620°C in a stream of argon. The temperature controller was set to the desired reaction temperature, in the same manner the timer was adjusted to the desired reaction time. At this point the GC is started and set to the desired conditions.

Once the reactor and the gas chromatograph have reached the desired operating conditions, the feed stock was injected directly into the reactor via a loaded syringe. After the reaction, the four port valve immediately opens ensuring that the reaction was terminated and the entire product stream sent on-line to the analytical equipment via a pre-heated vacuum box chamber.

### **2.4 Analysis**

The riser simulator operates in conjunction with a series of sampling valves that allow, following a predetermined sequence, one to inject reactants and withdraw products in short periods of time. The products were analyzed in an Agilent 6890N gas chromatograph with a flame ionization detector and a capillary column INNOWAX, 60-m cross-linked methyl silicone with an internal diameter of 0.32 mm.

### 3. Results and Discussions

Catalytic experiments involving three methyl benzenes (toluene, *m*-xylene, and 1,2,4-trimethyl benzene) were performed in a riser simulator over two different FCC catalysts (FCC-Y and FCC-Z). Experiments were carried out at catalyst/reactant ratio of 5 (weight of catalyst = 0.81g, weight of reactant injected = 0.162g); residence times of 3, 5, 7, 10, 13 and 15 s; and temperatures of 400, 450 and 500°C. During the course of the investigation, a number of runs were repeated to check for reproducibility in the conversion results, which was found to be excellent. Typical errors were in the range of  $\pm 2\%$ .

#### 3.1 Catalyst Characterization

Zeolite catalysts for use in fluidized-bed reactors are often incorporated in amorphous matrix to achieve the desired fluidization of the catalyst particles. As a result, the determination of the crystallinity and phase purity of the zeolite samples in the presence of this matrix is important in catalytic reactions. The results of the catalyst characterization are presented in **Table 1**. The amount of desorbed NH<sub>3</sub> (total acidity) and the measured BET surface area are summarized in the table. The XRD patterns of the catalysts (**Fig. 2**) are in agreements with those reported in the literature, without the presence of extraneous peaks.

#### 3.2 Disproportionation of Toluene

FCC-Y zeolite was used to convert toluene. However, no transformation of toluene into xylenes was observed for this catalyst steamed at 760°C for 5 hr. This result may be attributed to the low acidity of the steamed Y-zeolite catalyst (0.033mmol/g). **Table 2** shows the conversions of toluene at different reaction conditions using FCC-Y.

FCC-Z was also used in the disproportionation reaction of toluene. Similar to the FCC-Y, FCC-Z was not active and unable to transform toluene into xylenes. This behavior can also be attributed to the low acidity of the zeolite catalyst which is still lower than the minimum value required to transform toluene into xylenes. **Table 3** shows the conversions of toluene for different reaction conditions using FCC-Z.

It important to mention that when the reaction temperature was raised to 550°C and reaction time to 15 sec, the toluene conversion increased to 5.5 %. The products at these conditions are 46 % benzene, 50 % xylenes and remaining are trimethylbenzenes (TMBs).



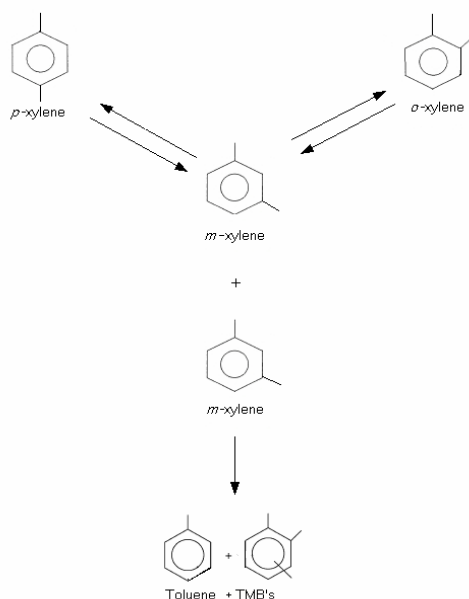
Since no gases were detected, it can be concluded that hydrodealkylation reaction has not taken place. It is also relevant to report that the xylenes distribution is as follows; *p*-xylene=0.734, *m*-xylene=1.405 and *o*-xylene=0.64. Hence, *p*-/*o*-xylene=1.15 > than the equilibrium value of 1.

Several more experiments have been conducted using both FCC-Z and FCC-Y at both 550 and 450°C to ascertain the similarity of the results in toluene conversion over these catalysts despite the huge difference in their acidities. However, our results still showed that both catalysts are almost inactive in converting toluene under our experimental conditions. In fact, the new data are quite in agreement with the results in **Tables 2** and **3**. Consequently, despite the high acidity in FCC-Z, the toluene conversion is still below expectation.

However, on a non-steamed Y-zeolite with 0.5 mmol/g acidity, more appreciable toluene conversion was found. The acidity of this catalyst was found to be much higher than the steamed zeolite. It can be concluded that at FCC conditions toluene is almost non-reactive, and higher acidity is needed to push this molecule to react.

### 3.3 *m*-Xylene Transformation Reactions

*m*-xylene isomerization (I) and disproportionation (D) have been used for characterization of acidic zeolites. *m*-xylene isomerizes to the *para* and *ortho* isomers and can disproportionate into trimethylbenzenes (TMBs) and toluene as illustrated in Scheme 1.



Scheme1

Both the isomerization and disproportionation reactions have been reported to be catalyzed by Brønsted acid sites, and disproportionation being a bimolecular reaction has been established to require higher concentration of acid sites [6].

Reaction results of *m*-xylene over FCC-Y and FCC-Z at different reaction temperatures and contact times are presented in **Tables 4 and 5** respectively. Disproportionation of *m*-xylene produces toluene and trimethylbenzenes whereas isomerization gives *o*- and *p*-xylene isomers. Only minor amount of benzene and tetramethylbenzene (TeMB) was found in the reaction products. It is observed from both **Tables 4 and 5**, conversion of *m*-xylene increases with reaction time for all temperatures studied. This is consistent with physical principles as the larger residence times offer an increased opportunity for the molecule to be reacted further.

The effect of temperature on *m*-xylene conversion is also reported in **Tables 4 and 5** over FCC-Y and FCC-Z respectively. At 15s, for the FCC-Y catalyst (**Table 4**), the conversion increased from 14.69% at 400°C to 23.37% at 450°C, an increase of about 59%. However, the conversion only increased from 23.37% at 450°C to about 29.14% at 500°C, an increase of only about 25%. This phenomenon of reduced increases in conversion as the temperature rises has also been observed in the FCC-Z catalyst (**Table 5**) where the conversion rose from 18.44% at 400°C to 26.66% at 450°C and then to 30.48% at 500°C, corresponding to relative increases in conversion of 44.6% and 14.3% respectively.

Comparison between the catalytic conversions of *m*-xylene attained over the two FCC catalysts at 7 and 15s reaction times are represented in **Figures 3a & 3b**. Over all the temperature studied, FCC-Z consistently shows higher conversions than FCC-Y for all reaction times. This goes to show that acidity plays a very important role in *m*-xylene transformation.

Disproportionation reaction requires two molecules of xylene reactants as bulky bimolecular transition state intermediates. As a result, disproportionation is significant on large pore zeolites that can accommodate these intermediates. ZSM-5 zeolites with smaller pore size are not expected to accommodate these intermediates of disproportionation pathway. **Table 4** shows that isomerization is about 1.6 times greater than disproportionation over the FCC-Y zeolite at 3% conversion and 400°C. Over the FCC-Z catalyst, isomerization was found to be only about 1.3 times greater than disproportionation at 400°C (**Table 5**). Furthermore, at 25% conversion and 500°C over FCC-Y, the I/D ratio is 0.7 while over FCC-Z is about 0.93. At 20% conversion and 450°C over FCC-Y, the I/D

ratio is 0.8 while over FCC-Z is about 1.2. This shows that FCC-Y produces more disproportionation than FCC-Z.

Collins et al. [28] reported that for both *meta*- and *para*-xylene isomerization and disproportionation over LaY catalyst, isomerization is 1.6-1.7 times greater than disproportionation. This is consistent with our findings. The isomerization to disproportionation (I/D) ratio decreases as conversion increases, it also decreases with reaction temperature. This observation is in agreement with the fact the disproportionation requires higher activation energy than isomerization. ZSM-5 with small pore size does not have enough space for the disproportionation intermediates, hence the lower I/D ratios. Similar to the FCC-Y, the (I/D) ratio decreases with conversion and reaction temperature.

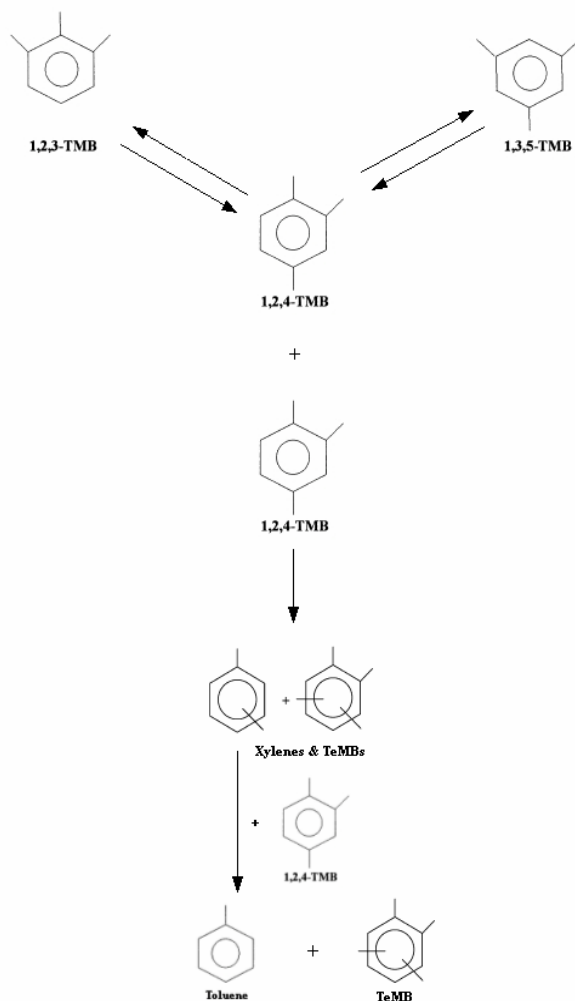
Toluene to trimethylbenzene distributions at various conversion levels over the two FCC catalysts are shown in **Tables 4 and 5**. As depicted in these tables, T/TMBs ratio is higher than the stoichiometric ratio of 1.0 for the two catalysts. The higher ratio of T/TMBs could be due to the slow desorption rate of trimethylbenzene isomers. In addition, since TMBs are necessary intermediates for coke formation, conversion of TMBs to coke may also serve as explanation for the low TMBs in relation to toluene. [29,30]

xylene transformation generally gives more 1,3,5-trimethylbenzenes than 1,2,3-trimethylmethylbenzene. The distribution of 1,3,5-to1,2,3-isomer over the two catalysts are presented in **Tables 4 and 5**. Over the FCC-Y, the ratio of 1,3,5-to 1,2,3-isomer lies between 3 and 3.5 at 400°C, which decreased to 2.7 at 450°C and ratio further decreased to 2.3 at 500°C. The ratio is a strong function of temperature and does not seem to change with *m*-xylene conversion. Similar behavior is observed over the FCC-Z (**Table 5**) in which the ratio of 1,3,5-TMB/1,2,3-TMB decreased from 3.3 (at 400°C) to 2.5 (at 450°C), and further decreased to 2.4 at 500°C. Similar values of the ratio of these two isomers have been reported [31,32] over 1,2,4-TMB.

### **3.4 1,2,4-Trimethylbenzene Transformation Reactions**

The results of transformation reaction of 1,2,4-TMB over FCC-Y and FCC-Z at different reaction temperatures and contact times are presented in **Tables 6 and 7** respectively. The experimental results show that isomerization, disproportionation and transalkylation reactions are taking place. The disproportionation reaction involves the formation of xylenes and tetramethylbenzenes (TeMB) from 2 moles of 1,2,4-TMB.

Subsequently, the xylenes (one of the disproportionation product) react with the TMB to form a transalkylation product toluene as illustrated in scheme 2.



Scheme 2

The data from the isomerization reaction show that higher amounts of 1,3,5-TMB were found as compared to the 1,2,3-TMB. Furthermore, three different isomers of tetramethylbenzenes (TeMB) were detected (1,2,4,5-TeMB, 1,2,3,5-TeMB and 1,2,3,4-TeMB). Benzene and pentamethylbenzene (PeMB) have been found to be negligible. Only minor amount of gaseous products was formed, indicating negligible dealkylation in our reaction condition. The experiments also suggest that the distribution of the xylenes and tetramethylbenzenes in the disproportionation products follow closely the values reported in the literature [21, 31, and 32].

**Tables 6** and **7** also showed that conversion of 1,2,4-TMB increases with temperature as well as with reaction time. At 15s, for the FCC-Y catalyst (**Table 6**), the

conversion increased from 33.25% at 400°C to 35.65% at 450°C, and subsequently to 35.73% at 500°C. Similarly, over the FCC-Z catalyst the conversion rose from 25.27% at 400°C to 27.0% at 450°C and then to 29.52% at 500°C. Comparison between the catalytic conversions of 1,2,4-TMB attained over the two FCC catalysts at 7 and 15s reaction times are represented in **Figures 4a & 4b**. Over the 400-500°C temperature range studied, FCC-Y consistently shows higher conversions than FCC-Z. This is despite the fact that the acidity of the FCC-Z catalyst is almost 7 times higher than that of the FCC-Y. As opposed to *m*-xylene, this shows that weaker acid sites are sufficient for 1,2,4-TMB transformation reactions.

Unity of xylene-to-tetramethylbenzene (X/TeMB) molar ratio should be obtained if there is no secondary transalkylation or dealkylation [31]. **Tables 6 and 7** show xylene-to-tetramethylbenzene (X/TeMB) distributions at various conversion levels over the two FCC catalysts. As depicted in these tables, X/TeMB ratio is higher than the stoichiometric ratio of 1.0 for both the two catalysts. These results are in agreement with the results of Atias et al. [20] who found increased amounts of xylenes over TeMBs. The higher ratio of X/TeMBs indicates that either secondary transalkylation or dealkylation is taking place. Dealkylation reaction was found to be inconsequential due to the very small amount of gases observed. Further analysis of the product mixture has shown that toluene yield (which might come from the transalkylation of xylenes with trimethylbenzenes) is increased at higher levels of conversion. With increased toluene yield at high conversions, toluene does not appear to be reacting with TeMB to further produce xylenes. TeMB may then have been trapped in micropores as coke precursors to account for the excess xylenes in relation to TeMB. This behavior is similar to T/TMB in *m*-xylene conversion. And it can also be attributed to the higher desorption rates of xylenes as compared to tetramethylbenzenes.

1,2,4-TMB can simultaneously undergo isomerization and disproportionation reactions. Again, **Tables 6 and 7** show that the isomerization to disproportionation (I/D) ratio lies between 0.3 and 0.4 at all conversion levels over the two catalysts. This indicates that 1,2,4-TMB preferentially undergoes disproportionation as compared to isomerization (approx. 3 times greater) in both FCC-Y and FCC-Z.

Experimental results for Isomerization reaction (**Tables 6 and 7**) show that higher amounts of 1,3,5-TMB were found as compared to the 1,2,3-TMB even though the 1,2,3-isomer has a smaller molecular size than 1,3,5-TMB [35]. However, 1,3,5-TMB is thermodynamically favored over the 1,2,3-isomer. It may be inferred therefore that 1,2,4-

TMB transformation is thermodynamically controlled. The ratio of 1,3,5- to-1,2,3-isomer over the FCC-Y is about 2.0 and is invariant with conversion. As for the FCC-Z, the ratio of 1,3,5-/1,2,3-trimethylbenzene lies between 1.8 to 2.0, and decreases slightly with temperature. Wang et al. [31] reported a thermodynamic equilibrium value of 2.7 for the 1,3,5-/1,2,3-trimethylbenzene ratio at 344°C.

### 3.5 *Comparison of the results of transformation reactions of 1,2,4-TMB, m-Xylene and Toluene*

#### 3.5.1 *Reactivity*

Conversions of these reactants are plotted versus reaction time over both FCC-Y and FCC-Z catalyst in Figures **5a**, **5b**, **6a** & **6b**. At the lower temperature of 400°C (Figs. 11a & 11b), the plots clearly show that trimethylbenzene is much more reactive than both *m*-xylene and toluene, while *m*-xylene is more reactive than toluene under our present experimental conditions. This is true for both the FCC-Y and FCC-Z zeolite catalysts. The much higher reactivity of the trimethylbenzene may be due to the higher number of methyl group attached to its benzene ring which enables it to undergo much deeper reactions than the others. Wang et al. [31] reported that mixing trimethylbenzene into toluene could increase its conversion.

At higher temperatures (450°C and above), the trimethylbenzene still has higher reactivity than the other molecules over the FCC-Y (**Fig. 6a**). However, over the FCC-Z, the reactivity of the trimethylbenzene and *m*-xylene are now comparable. Conversion of the 1,2,4-TMB to coke may serve as an explanation why its reactivity slowed down. Furthermore, Cejka et al. [21] measured the diffusion coefficients of 1,2,4-TMB, *m*-xylene and others over known zeolites, and found that the values of the diffusion coefficient were decreasing in the order *m*-xylene  $\gg$  1,2,4-TMB. It may have been that due to an increase in the rate of diffusion of *m*-xylene at high temperatures, coupled with the strong diffusion limitations the FCC-Z zeolite presents for large trimethyl benzene molecules, all contribute to similarity in reactivity of the trimethylbenzene and *m*-xylene at 500°C.

#### 3.5.2 *Isomerization versus Disproportionation*

The ratio of the rates of isomerization to disproportionation (I/D) is useful for providing information relating to zeolite pore size. Since disproportionation requires a bimolecular reaction, larger pore systems that can accommodate the required transition state

give more disproportionation [7]. Plots of isomerization to disproportionation (I/D) ratio are shown in **Figures 7a & 7b** over the two catalysts to illustrate the dependence of the (I/D) ratio on the reactant conversions at 500°C.

The results of this study have shown that for *m*-xylene transformation over our two FCC catalysts, isomerization is 0.7-1.0 times greater than disproportionation at 500°C. It is 1.6 times greater than disproportionation over the FCC-Y zeolite at 3% conversion and 400°C (**Table 4**) and 1.3 times greater over FCC-Z at 400°C (**Table 5**). This clearly shows that the I/D ratio decreases with temperature and slightly change with conversion for the *m*-xylene transformation reaction.

However, isomerization to disproportionation ratio (I/D) for 1,2,4-TMB transformation reactions on the other hand indicates that 1,2,4-TMB preferentially undergoes disproportionation as compared to isomerization in both FCC-Y and FCC-Z. Disproportionation was found to be approximately 2.5 times greater than isomerization (I/D ratio = 0.4) at 500°C (**Fig. 7a & 7b**).

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

The *p*-Xylene to *o*-Xylene (P/O) ratio provides very good insights as well into the zeolite pore size. Larger values of the P/O ratio point to small pores while lower values tend to show existence of large pores. Generally, P/O ratio increases with both temperature and conversion. This behavior might be due to the increased coke deposition as temperature increases leading to the narrowing of the zeolite channel thereby giving *p*-xylene (kinetic diameter,  $d_k = 0.58\text{nm}$ ) advantage over *o*-xylene ( $d_k = 0.68\text{nm}$ ).

The ratios of *para*- to *ortho*-xylene (P/O) in the product mixture are presented in **Figures 8a & 8b** over FCC-Y and FCC-Z respectively at 500°C. Over the FCC-Y catalyst, the P/O ratio increases slightly as conversion increases for the *m*-Xylene transformation. It increases from a value of 0.8 at 10% conversion to a value of 1.0 at 30% conversion. Thus, below 30% conversion, P/O ratio over the FCC-Y is well below the equilibrium value of 1.0. FCC-Z on the other hand showed *para*-selectivity for the *m*-xylene transformation as its P/O ratio averages 1.3 over the whole conversion range. This value is very consistent with the smaller ZSM-5 pores giving advantage to *p*-xylene over *o*-xyelene.

However for 1,2,4-TMB transformation, the P/O ratio lies between 0.7 and 0.8 and its change with conversion is very minute. Similar ratios were obtained by Park et al. [32] over HMCM-22 at 350°C. This shows that 1,2,4-TMB produces more *o*-xylene than *p*-

xylene at all conversion levels, and are therefore not *para*-selective as they undergo the 1,2,4-TMB transformation reaction. The mechanism based on biphenyl-methane carbonium ion intermediates [34] has been proposed to explain this phenomenon. Furthermore, our results show that P/O from isomerization reaction seems to be higher than P/O resulting from disproportionation. This might suggest that isomerization favors *p*-xylene while disproportionation favors *o*-xylene.

#### 3.5.4 1,3,5-TMB to 1,2,3-TMB ratio

The distribution of trimethylbenzenes can also provide useful insights into the zeolite pore structure. Zeolites with large cages generally favor the bigger 1,3,5-TMB molecule, while small pore zeolites favor 1,2,3-TMB isomer. Experimental results for both *m*-xylene and 1,2,4-TMB transformation reactions have shown that higher amounts of 1,3,5-TMB were found as compared to the 1,2,3-TMB. However, both the two FCC catalysts gave higher ratio of 1,3,5-to-1,2,3 during the *m*-xylene transformation reaction as compared to that of 1,2,4-TMB.

**Figures 9a & 9b** depict the relationship between the 1,3,5-TMB/1,2,3-TMB ratio and conversion. For the *m*-xylene transformation reaction, the FCC-Y gave a ratio of about 2.35 while a ratio of about 2.4 was obtained over the FCC-Z at 500°C. The two zeolites gave 1,3,5-TMB/1,2,3-TMB ratio of about 2.0 for the 1,2,4-TMB transformation under our experimental conditions, which deviates from the thermodynamic equilibrium value of 2.7 over USY at 350°C [35].

#### 3.5.5 Effect of Zeolite Structure

The shape and size of zeolite structure plays a crucial role in determining isomerization to disproportionation ratio, reaction isomer distributions and P/O ratio among others, through the restricted transition state and reactant shape selectivities. Two FCC zeolite catalysts, (FCC-Y & FCC-Z) have been used in this study with different acidity and pore size as presented in **Table 1**. The ZSM-5 based zeolite (FCC-Z) with pore size of 5-6Å presents strong diffusion limitations for large trimethyl benzene molecules. As a result diffusion into its pore is very slow, and conversions of trimethyl benzenes over ZSM-5 zeolites are lower as compared to large pore zeolites under similar reaction conditions like the FCC-Y [21]. This is evident from the results presented in **Fig. 4**.



Furthermore, trimethyl benzene disproportionation reaction results are completely different for medium pore ZSM-5 based zeolite (like FCC-Z) as compared to large pore zeolites (e.g. FCC-Y with pore size of about 7.4Å). The reaction proceeds within the zeolite channel in Y-zeolite due to its ability to accommodate the bimolecular reaction transition intermediates, thereby giving rise to higher rate of reaction as compared to ZSM-5. Therefore, in large pore zeolites, disproportionation is main pathway while for medium pore zeolites; isomerization seems to be the path of choice. The rate of isomerization to disproportionation (I/D) follows the order of the zeolite structure as follows: Y zeolite < ZSM-5.

*p*-xylene to *o*-xylene (P/O) ratio has been found to be much higher in ZSM-5 as compare to Y-zeolite for methyl benzene transformation, most especially *m*-xylene (**Figures 8a & 8b**). It has been suggested that the kinetic diameter of the transition for *m*- to *p*-xylene isomerization is smaller (0.62 nm) compared to that for *m*- to *o*-xylene (0.67 nm) [21]. This shows that *restricted transition state selectivity* controls the selectivity of *m*-xylene isomerization over ZSM-5 [14].

Acidity of zeolites also contributes significantly to the overall rate of reaction. However, reaction conditions most importantly reaction temperature and zeolite structure can alter the effect of acidity. As there cases where at some reaction conditions, zeolites with lesser acidity can give superior activity compared to those with higher acidity.

## 4. Conclusions

The following conclusions can be drawn from the catalytic transformation of the three methyl benzenes (*toluene*, *m-xylene*, and *1,2,4-trimethyl benzene*) over two FCC-zeolite catalysts in fluidized bed reactor (riser simulator) under the conditions of the experimental study:

1. The reactivity of the methyl benzenes was found to increase in the sequence: *toluene* < *m-xylene* < *1,2,4-trimethyl benzene*. This is attributed to the increase in the number of methyl group attached to the benzene. This is true at all temperatures over the FCC-Y zeolite catalyst. It is also true over the FCC-Z for low to moderate temperatures. However at 450°C and above, the reactivity of *m-xylene* was found to be comparable to that of 1,2,4-TMB.

2. The results show that catalytic activity of methyl benzene transformation is very much influenced by the complex interplay between the zeolite system structure, kinetic diameter of reactants in relation to the zeolite channel diameter, reaction conditions and catalyst acidity. Higher acidity does not necessarily translate to higher activity, as there some certain reaction conditions where zeolites with lower acidity can give higher activity compared to those with higher acidity.

3. Investigation into the various ratios that provide useful insights into the pore structure of zeolite catalysts (I/D, P/O, 1,3,5-TMB/1,2,3-TMB) show that the *m-xylene* transformation produces more isomerization products than disproportionation. While on the other hand, 1,2,4-TMB transformation gave more disproportionation compared to isomerization. Furthermore, the *m-xylene* reaction consistently gave higher P/O & 1,3,5-TMB/1,2,3-TMB ratios than the 1,2,4-TMB reaction over two FCC catalysts.

4. The present results suggest that isomerization reaction favors *p-xylene* while disproportionation favors *o-xylene*.

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Table 1: Characterization of used Catalysts

Catalyst	Acidity (mmol/g)	Lewis sites %	Bron sites %	Surface Area ( m <sup>2</sup> /g)	Catalyst Type	Na <sub>2</sub> O wt %
FCC-Z	0.233	44	56	70	ZSM-5	Negligible
FCC-Y	0.033	35	65	150	Y-Zeolite	Negligible

Table 2: Toluene conversions (%) at different reaction conditions over FCC-Y

Temp (°C)/ time (s)	Conversion (%)
<b>350</b>	
5	0.26
10	0.353
<b>400</b>	
5	0.39
10	0.517
<b>450</b>	
5	0.56
10	0.84
<b>500</b>	
5	0.89
10	1.65

Table 3: Toluene conversions (%) at different reaction conditions over FCC-Z

Temp (°C)/ time (s)	Conversion (%)
<b>350</b>	
3	-
7	-
10	0.33
<b>400</b>	
3	-
7	-
10	0.512
<b>450</b>	
3	-
7	0.634
10	0.915
<b>500</b>	
3	0.45
7	0.86
10	1.62
15	3.28
<b>550</b>	
3	1.01
7	2.47
10	3.65
15	5.50



Table 4: Product distribution (wt %) at various reaction conditions for *m*-xylene transformation over FCC-Y

Temp (°C)/ time (s)	Conv. (%)	Gas	Benzene	<i>m</i> - xylene	<i>p</i> - xylene	<i>o</i> - xylene	<b>TI*</b>	Toluene	<i>1,3,5</i> TMB	<i>1,2,4</i> TMB	<i>1,2,3</i> TMB	TeMB's	<b>TD**</b>
<b>400</b>													
3	3.80	-	-	96.21	0.96	1.29	2.25	0.81	0.17	0.41	0.05	-	1.44
5	6.59	-	-	93.41	1.57	1.86	3.43	1.64	0.38	0.92	0.13	-	3.07
7	7.022	-	-	92.98	1.67	1.95	3.62	1.73	0.43	1.03	0.15	-	3.34
10	9.6	-	-	90.42	1.99	2.35	4.34	2.59	0.69	1.62	0.20	0.05	5.10
15	14.69	-	0.06	85.31	3.26	3.49	6.75	3.78	1.03	2.50	0.33	0.17	7.64
<b>450</b>													
3	6.94	-	0.05	93.06	1.57	1.89	3.46	1.77	0.38	1.00	0.14	0.05	3.29
5	9.26	-	0.08	89.75	2.23	2.51	4.74	2.71	0.63	1.62	0.24	0.15	5.20
7	12.6	-	0.11	87.41	2.64	2.93	5.57	3.39	0.82	2.11	0.31	0.21	6.63
10	17.7	-	0.15	82.31	3.66	3.90	7.56	4.78	1.20	3.09	0.46	0.38	9.53
15	23.37	-	0.18	76.63	4.92	5.07	9.99	6.26	1.61	4.14	0.63	0.51	12.64
<b>500</b>													
3	8.02	-	0.11	91.98	1.67	2.01	3.68	2.12	0.46	1.24	0.19	0.15	4.01
5	12.11	-	0.18	87.88	2.42	2.72	5.14	3.33	0.76	2.04	0.33	0.27	6.46
7	15.6	-	0.23	84.44	3.03	3.31	6.34	4.32	1.02	2.73	0.43	0.42	8.50
10	21.30	-	0.29	78.70	4.13	4.35	8.48	5.93	1.44	3.87	0.61	0.61	11.85
15	29.14	0.07	0.40	70.87	5.59	5.77	11.36	8.14	2.01	5.37	0.87	0.87	16.39

\*TI – Total isomerization

\*\*TD – Total Disproportionation

Table 5: Product distribution (wt %) at various reaction conditions for *m*-xylene transformation over FCC-Z

Tem p (°C)/ time (s)	Conv (%)	Gas	Benzene	<i>m</i> - xylene	<i>p</i> - xylene	<i>o</i> - xylene	<b>TI*</b>	Toluene	<i>1,3,5</i> TMB	<i>1,2,4</i> TMB	<i>1,2,3</i> TMB	TeMBs	<b>TD*</b>
<b>400</b>													
3	3.87	-	-	96.13	1.26	0.91	2.17	0.80	0.25	0.58	0.07	-	1.70
7	9.13	-	-	90.87	3.20	1.91	5.11	1.87	0.55	1.33	0.17	0.09	3.92
10	13.21	-	0.06	86.79	4.09	2.81	6.90	2.92	0.81	2.04	0.29	0.19	6.06
13	16.66	-	0.06	83.34	5.96	3.48	9.44	3.32	0.96	2.39	0.31	0.18	6.98
15	18.44	-	0.06	81.56	6.75	3.89	10.64	3.59	1.04	2.59	0.34	0.18	7.56
<b>450</b>													
3	7.96	-	0.05	92.04	2.42	1.78	4.20	1.74	0.46	1.20	0.18	0.12	3.58
7	15.84	-	0.09	84.16	4.91	3.45	8.36	3.47	0.91	2.40	0.36	0.25	7.14
10	21.39	0.04	0.12	78.61	6.72	4.66	11.38	4.59	1.21	3.19	0.48	0.38	9.47
13	24.99	0.05	0.15	75.01	7.70	5.34	13.04	5.51	1.43	3.78	0.56	0.45	11.28
15	26.66	0.05	0.18	73.34	8.08	5.58	13.66	5.96	1.56	4.12	0.61	0.51	12.25
<b>500</b>													
3	8.66	-	0.09	91.34	2.30	1.78	4.08	2.12	0.56	1.40	0.22	0.18	4.30
7	17.30	0.05	0.18	82.70	4.36	3.53	7.89	4.31	1.06	2.88	0.46	0.46	8.71
10	24.30	0.05	0.25	75.70	6.28	4.99	11.27	5.99	1.46	4.00	0.64	0.63	12.09
13	27.10	0.09	0.26	72.91	7.01	5.56	12.57	6.60	1.65	4.47	0.72	0.69	13.44
15	30.48	0.13	0.32	69.52	8.21	6.26	14.47	7.26	1.79	4.90	0.77	0.73	14.72

\*TI – Total isomerization

\*\*TD – Total Disproportionation

Table 6: Product distribution (wt %) at various reaction conditions for *1,2,4-Trimethylbenzene* transformation over FCC-Y

Temp (°C)/ time (s)	Conv. (%)	Gas	Benzene	<i>1,3,5</i> - TMB	<i>1,2,3</i> - TMB	<b>TI*</b>	<i>p</i> - xylene	<i>m</i> - xylene	<i>o</i> - xylene	Toluen e	TeMB's ( <i>1,2,3,4</i> - , <i>1,2,3,5</i> -, & <i>1,2,4,5</i> )	<b>TD**</b>
<b>400</b>												
3	8.12	-	-	1.33	0.65	1.99	0.55	1.31	0.82	0.30	2.09	5.07
5	12.64	-	-	2.04	0.99	3.03	0.89	2.10	1.30	0.47	3.73	8.49
7	17.40	-	-	2.76	1.34	4.10	1.23	2.89	1.78	0.64	5.48	12.02
10	24.00	0.06	-	3.80	1.84	5.64	1.68	3.98	2.47	0.84	7.99	16.96
13	29.80	0.09	-	4.72	2.27	6.99	2.08	4.92	3.03	1.03	10.22	21.28
15	33.25	0.11	0.04	5.22	2.5	7.72	2.32	5.48	3.37	1.15	11.55	23.87
<b>450</b>												
3	9.90	-	-	1.67	0.82	2.49	0.67	1.54	0.94	0.38	2.75	6.28
5	15.64	0.07	-	2.60	1.26	3.86	1.07	2.48	1.49	0.60	4.80	10.44
7	20.00	0.10	-	3.31	1.60	4.91	1.38	3.19	1.90	0.77	6.42	13.66
10	26.88	0.14	-	4.44	2.12	6.56	1.88	4.33	2.55	1.04	8.97	18.77
13	32.40	0.16	0.05	5.31	2.53	7.84	2.25	5.21	3.06	1.23	11.01	22.76
15	35.65	0.25	0.06	5.86	2.80	8.66	2.46	5.71	3.37	1.35	12.20	25.09
<b>500</b>												
3	11.48	0.09	-	1.96	0.97	2.93	0.78	1.76	1.02	0.49	3.25	7.30
5	16.22	0.15	-	2.74	1.34	4.08	1.13	2.55	1.46	0.71	4.90	10.75
7	21.44	0.21	-	3.61	1.76	5.37	1.50	3.39	1.94	0.92	6.72	14.47
10	28.20	0.33	0.05	4.73	2.29	7.02	1.98	4.50	2.56	1.23	9.06	19.33
13	32.62	0.44	0.06	5.44	2.63	8.07	2.31	5.26	2.97	1.45	10.50	22.49
15	35.73	0.47	0.07	5.91	2.85	8.76	2.53	5.79	3.29	1.58	11.51	24.70

\*TI – Total isomerization

\*\*TD – Total Disproportionation

Table 7: Product distribution (wt %) at various reaction conditions for 1,2,4-Trimethylbenzene transformation over FCC-Z

Temp (°C)/ time (s)	Conv (%)	Gas	Benzene	1,3,5 TMB	1,2,3 TMB	TI*	<i>p</i> - xylene	<i>m</i> - xylene	<i>o</i> - xylene	Toluen e	TeMB's (1,2,3,4-, 1,2,3,5-, & 1,2,4,5)	TD**
<b>400</b>												
3	7.95	-	-	1.25	0.63	1.88	0.45	1.12	0.66	0.22	2.51	4.96
5	10.90	0.06	-	1.66	0.86	2.52	0.66	1.59	0.97	0.31	3.63	7.16
7	13.80	0.07	-	2.00	1.06	3.06	0.87	2.08	1.30	0.38	4.82	9.45
10	19.56	0.09	-	2.78	1.51	4.29	1.26	3.03	1.95	0.52	7.17	13.93
13	22.96	0.10	-	3.19	1.76	4.95	1.50	3.60	2.35	0.58	8.60	16.63
15	25.27	0.12	0.05	3.43	1.92	5.35	1.68	3.97	2.58	0.65	9.45	18.33
<b>450</b>												
3	8.95	0.07	-	1.40	0.72	2.12	0.53	1.25	0.74	0.28	2.74	5.54
5	12.18	0.10	-	1.90	0.98	2.88	0.76	1.79	1.08	0.39	3.98	8.00
7	16.44	0.16	-	2.60	1.36	3.96	1.08	2.47	1.50	0.56	5.42	11.03
10	20.50	0.16	-	3.11	1.68	4.79	1.38	3.14	1.98	0.65	7.11	14.26
13	24.91	0.20	0.05	3.86	2.07	5.93	1.68	3.84	2.41	0.78	8.72	17.43
15	27.00	0.25	0.06	4.12	2.22	6.34	1.81	4.13	2.60	0.83	9.40	18.77
<b>500</b>												
3	9.62	0.12	-	1.55	0.80	2.35	0.62	1.40	0.81	0.37	2.81	6.01
5	14.37	0.18	-	2.31	1.20	3.51	0.96	2.17	1.27	0.54	4.47	9.41
7	18.13	0.23	-	2.94	1.56	4.50	1.22	2.77	1.67	0.68	5.80	12.14
10	23.29	0.29	0.05	3.78	1.99	5.77	1.60	3.61	2.17	0.87	7.65	15.90
13	27.33	0.42	0.07	4.49	2.37	6.86	1.91	4.28	2.56	1.05	8.90	18.70
15	29.52	0.44	0.08	4.79	2.57	7.36	2.06	4.60	2.77	1.13	9.54	20.10

\*TI – Total isomerization

\*\*TD – Total Disproportionation

## Figure Captions

- Figure 1: Schematic Diagram of the Riser Simulator
- Figure 2: X-ray Diffraction for the catalysts used in the study
- Figure 3: *m*-Xylene conversions at various temperatures **a)** 7-s reaction time; **b.)** 15-s reaction time
- Figure 4: 1,2,4-TMB conversions at various temperatures **a)** 7-s reaction time; **b.)** 15-s reaction time
- Figure 5: Reactivity comparisons between 1,2,4-TMB transformation (◆), *m*-xylene (□) and toluene (Δ) at 400°C over **a)** FCC-Y; **b)** FCC-Z
- Figure 6: Reactivity comparisons between 1,2,4-TMB transformation (◆), *m*-xylene (□) and toluene (Δ) at 500°C over **a)** FCC-Y; **b)** FCC-Z
- Figure 7: I/D ratio comparisons between 1,2,4-TMB transformation (◆) and *m*-xylene (□) at 500°C over **a)** FCC-Y; **b)** FCC-Z
- Figure 8: P/O ratio comparisons between 1,2,4-TMB transformation (◆) and *m*-xylene (□) at 500°C over **a)** FCC-Y; **b)** FCC-Z
- Figure 9: 1,3,5-TMB/1,2,3-TMB ratio comparisons between 1,2,4-TMB transformation (◆) and *m*-xylene (□) at 500°C over **a)** FCC-Y; **b)** FCC-Z

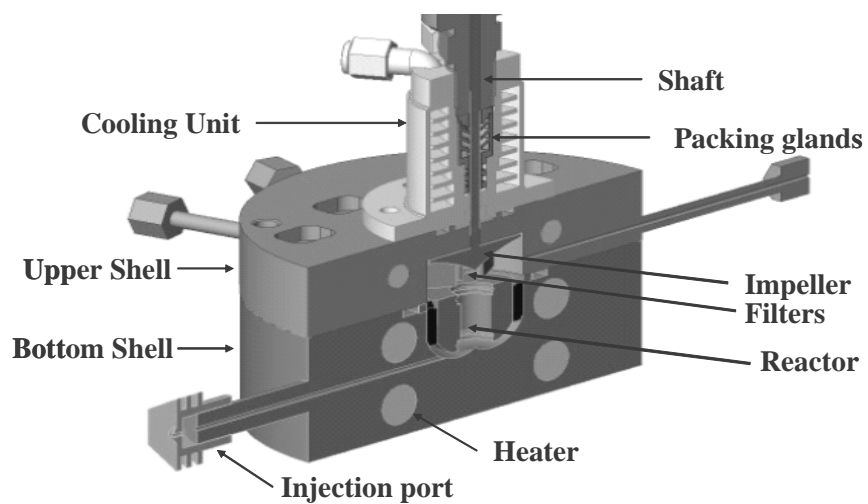


Figure 1: Schematic Diagram of the Riser Simulator

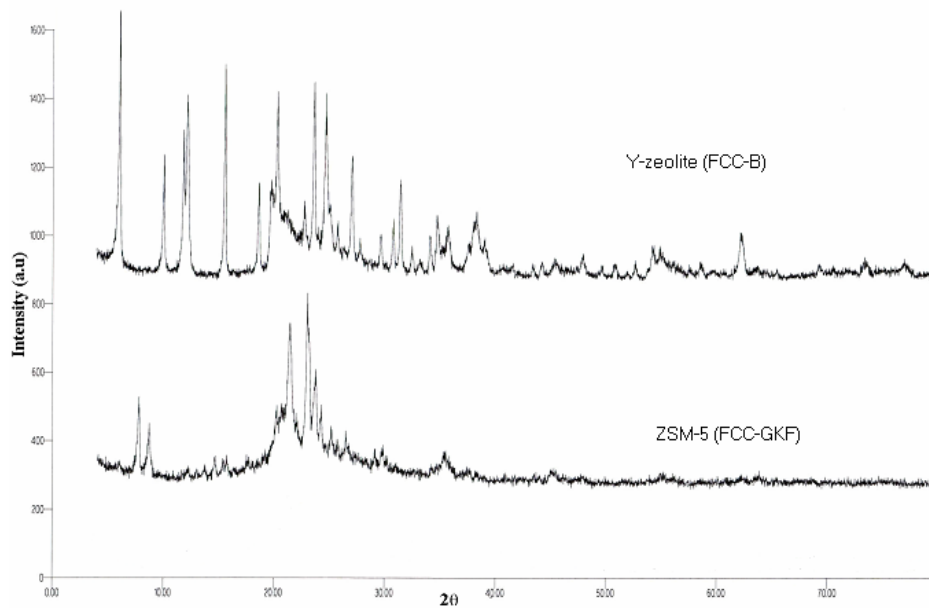


Figure 2: X-ray Diffraction for the catalysts used in the study

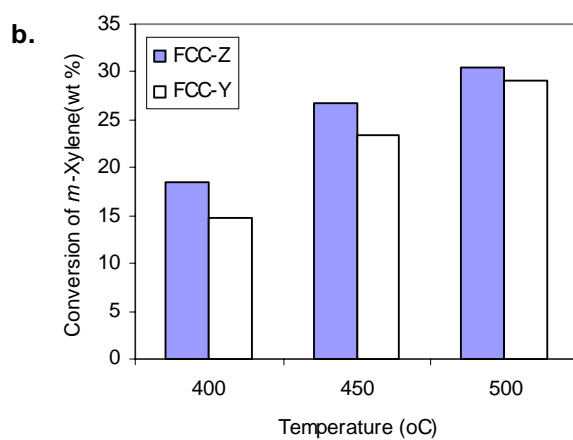
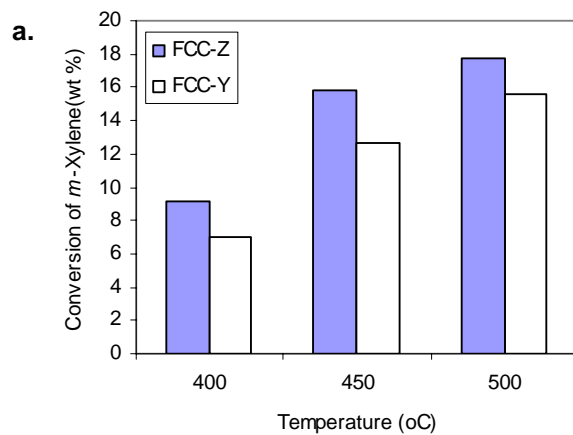


Figure 3: *m*-Xylene conversions at various temperatures **a)** 7-s reaction time; **b.)** 15-s reaction time

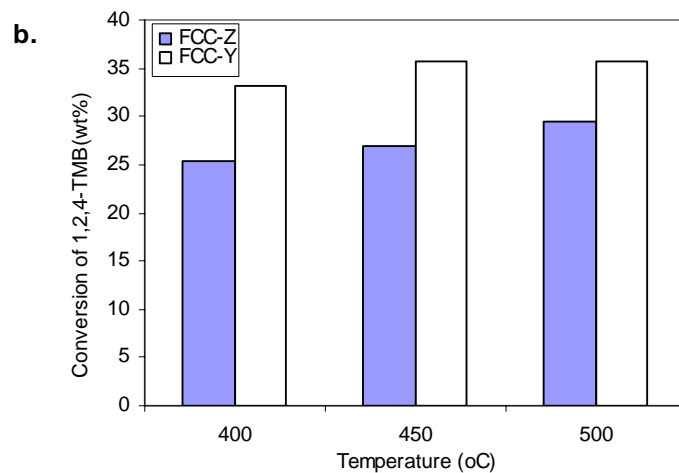
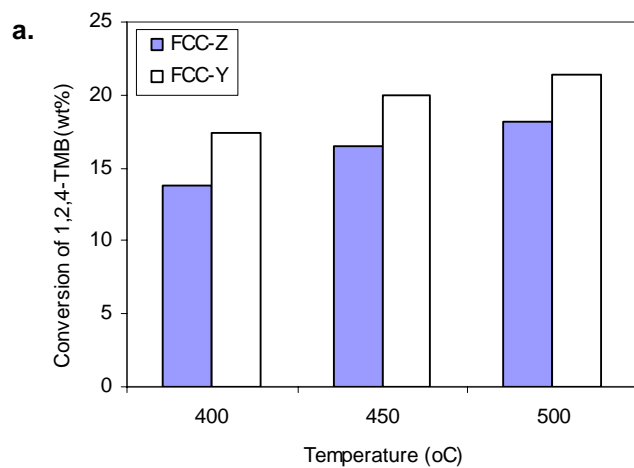


Figure 4: 1,2,4-TMB conversions at various temperatures **a)** 7-s reaction time; **b.)** 15-s reaction time



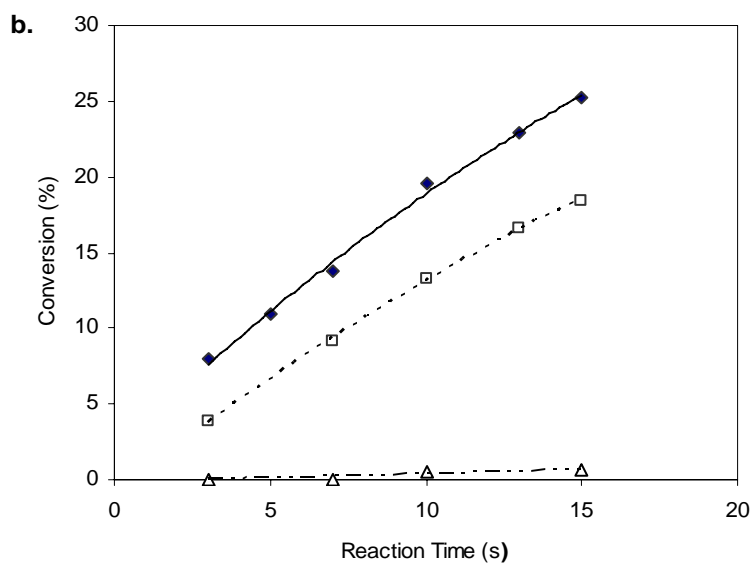
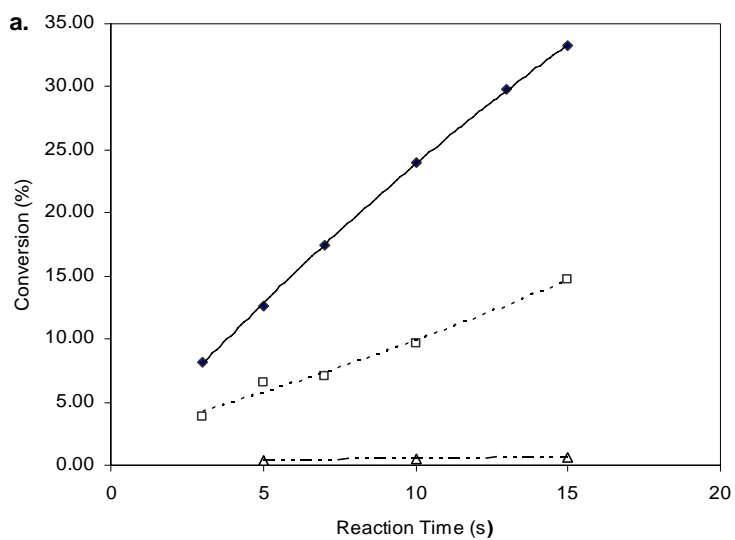


Figure 5: Reactivity comparisons between 1,2,4-TMB transformation ( $\blacklozenge$ ), *m*-xylene ( $\square$ ) and toluene ( $\triangle$ ) at 400°C over **a)** FCC-Y; **b)** FCC-Z

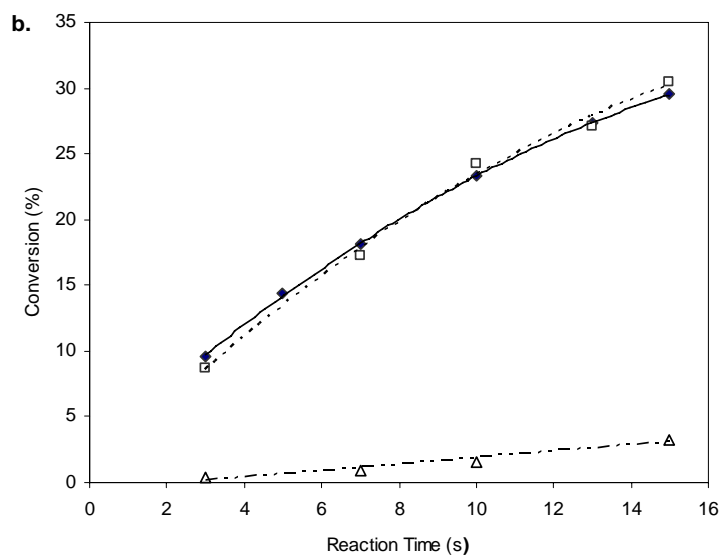
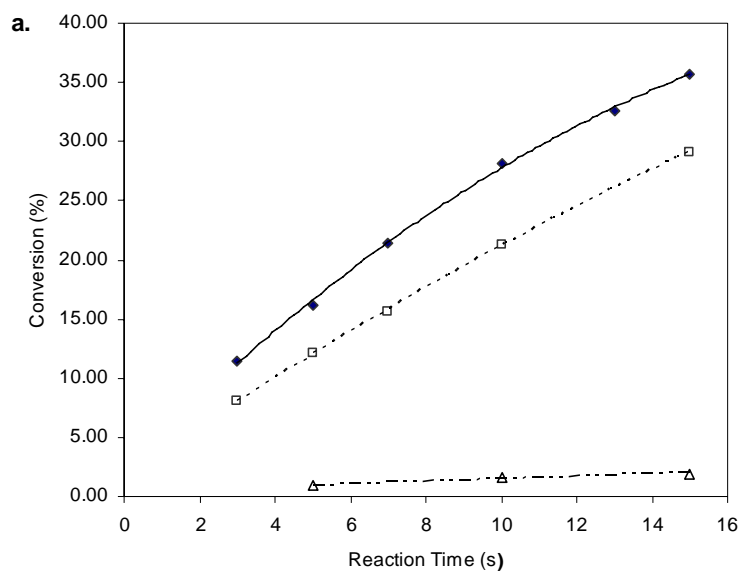


Figure 6: Reactivity comparisons between 1,2,4-TMB transformation ( $\blacklozenge$ ), *m*-xylene ( $\square$ ) and toluene ( $\triangle$ ) at 500°C over **a)** FCC-Y; **b)** FCC-Z

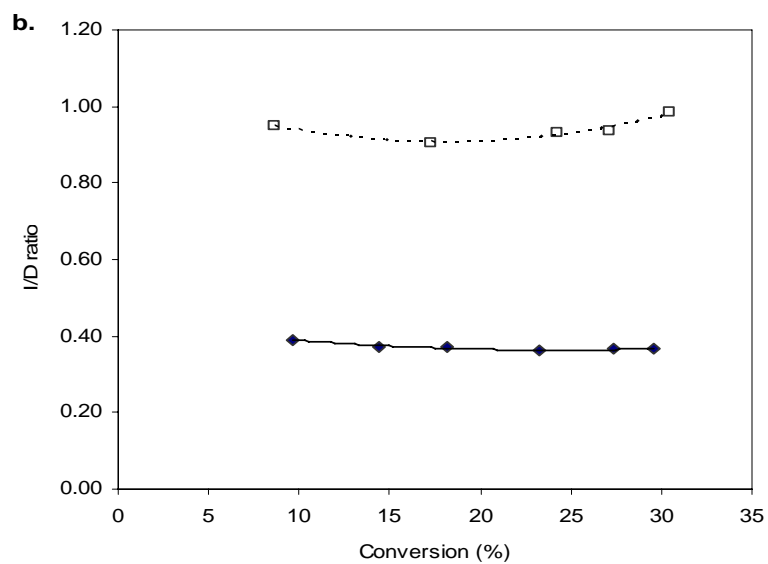
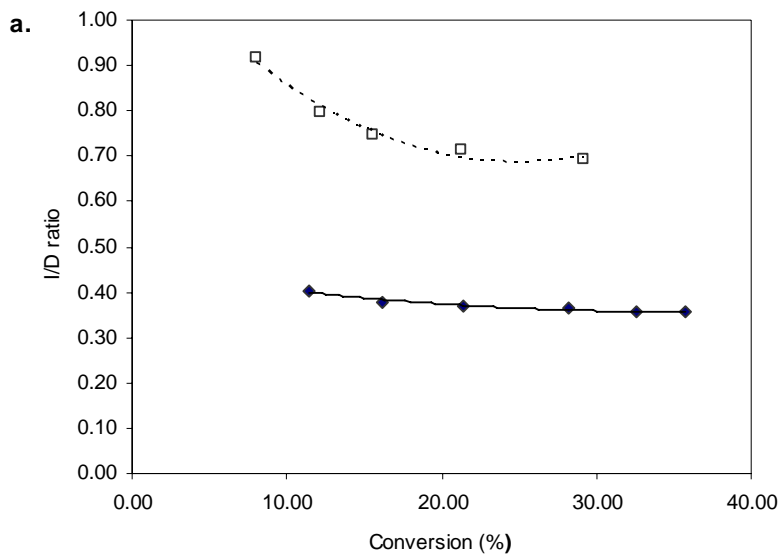


Figure 7: I/D ratio comparisons between 1,2,4-TMB transformation (◆) and *m*-xylene (□) at 500°C over **a)** FCC-Y; **b)** FCC-Z

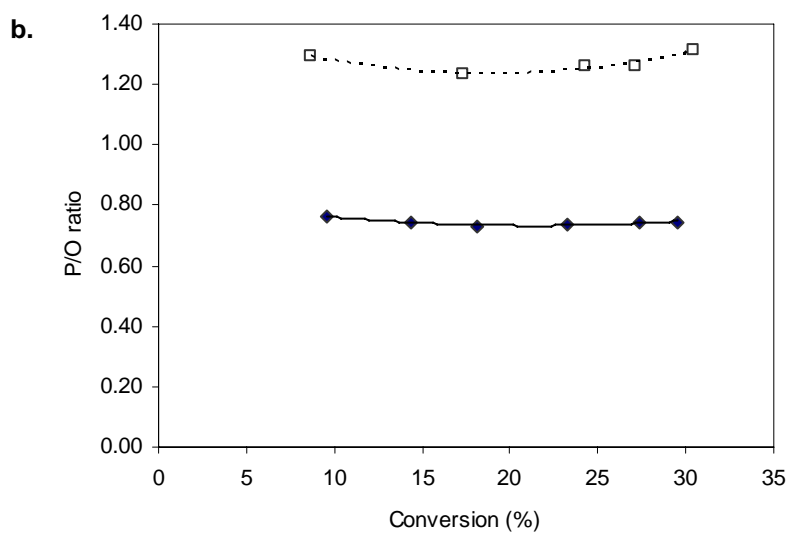
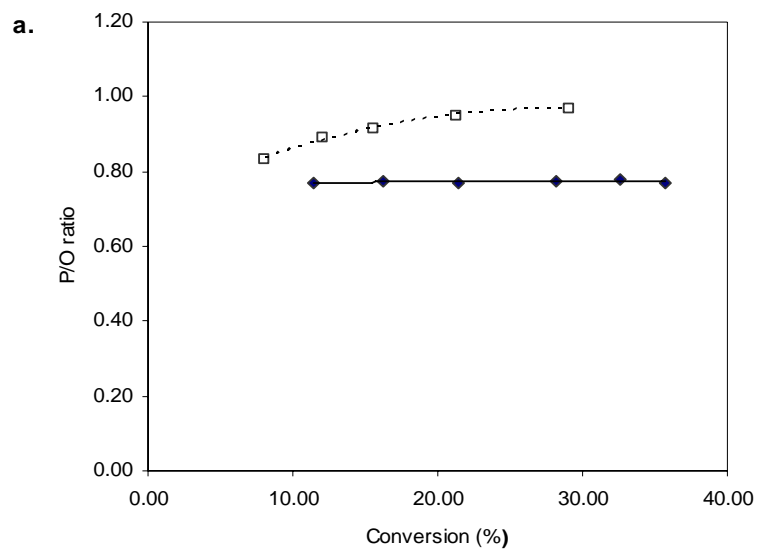


Figure 8: P/O ratio comparisons between 1,2,4-TMB transformation ( $\blacklozenge$ ) and *m*-xylene ( $\square$ ) at 500°C over **a)** FCC-Y; **b)** FCC-Z

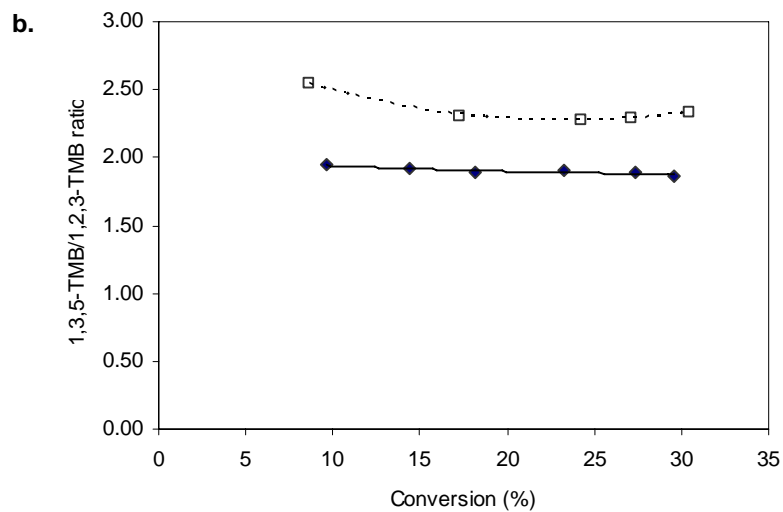
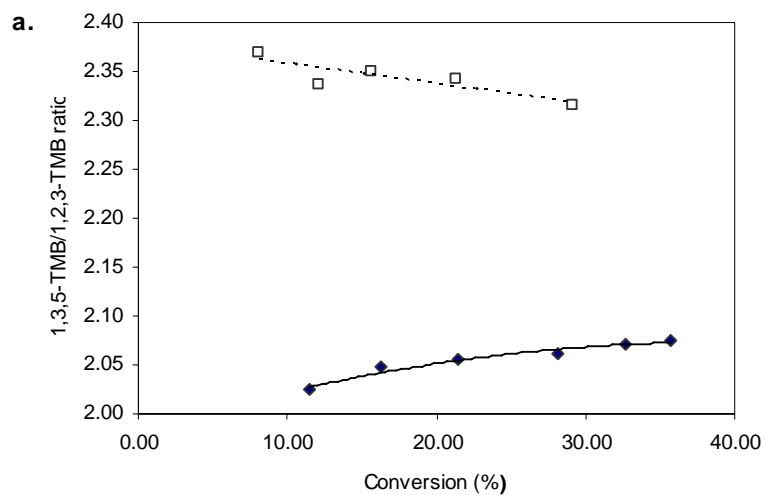


Figure 9: 1,3,5-TMB/1,2,3-TMB ratio comparisons between 1,2,4-TMB transformation (♦) and *m*-xylene (□) at 500°C over a) FCC-Y; b) FCC-Z