

CATALYTIC TRANSALKYLATION OF TRIMETHYLBENZENES WITH TOLUENE

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Abstract

Transalkylation of aromatic compounds catalysed by β -zeolite catalyst has been investigated. The study was basically oriented at the transformation of trimethylbenzenes, main source of which are C9⁺ fractions from steam cracking or reforming processes, into xylenes. The experimental data from transalkylation study were used for reaction & separation simulation discussing technological aspects of the production of xylenes via trimethylbenzene transalkylation.

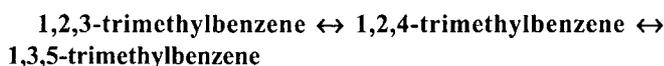
Key words: transalkylation, trimethylbenzenes, toluene, beta zeolite, modeling, experiment

Introduction

Research activities in the field of aromatics transformation, which can be observed during last few years [1-3], seem to be motivated mainly by improvement and modifications in ecological standards, which will lead to substantial decrease of aromatics content in liquid fuels. Consequently, a large excess of basic aromatics, first of all benzene and toluene, is expected in the world market. The recently published studies [2,3] were aimed at finding alternative routes to alkylaromatics utilisation in chemical industry. Basic source of aromatics are the steam cracking of heavy fractions and reforming of hydrocarbon fractions [4]. One of the possible transformation routes could be transalkylation and disproportionation of alkylated benzenes [5-9], an example represents reaction between toluene and trimethylbenzenes, which convert cheaper aromatics to more valuable xylenes which are important starting components for the industrial processes like the production of synthetic fibers, resins, plasticizers etc.

The products from transalkylation reactor should be consequently separated and the resulting xylene fraction purified. Therefore the rectification unit must be performed and unconverted starting components can be recycled back to the feed. Thus, the complex technological flowsheet cover not only chemical reactor and its specification but also technological aspects of xylene separation.

The desired reaction, i.e. transalkylation of trimethylbenzenes and toluene to xylenes, is accompanied by isomerisation of trimethylbenzenes (1,2,3-, 1,2,4- and 1,3,5-isomers) and xylenes (o-, m-, p- isomers). In addition, the disproportionation of trimethylbenzenes and toluene takes place in the reaction system too. Dealkylation of alkylbenzenes to low substituted aromates and aliphatic hydrocarbons can even be observed at higher reaction temperature. The parallel-consecutive reaction system is characterised by multiple chemical equilibrium. In case of trimethylbenzene and toluene feed the following individual reactions can be identified:



Disproportionation



Dealkylation (example)



Solid acid catalysts such e.g. beta zeolite [1,8] are usually recommended for transalkylation reaction. The first industrial process for alkylaromatics transalkylation is TransPlusTM, commercialized in 1997 [10].

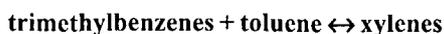
Experimental

A continuous packed bed tubular reactor of 40 mm inner diameter 1 m length was used to perform the experiments in this study, aimed at the transalkylation of trimethylbenzenes with toluene. The equimolar reaction mixture of hydrocarbons was continuously fed to reactor together with hydrogen in molar ratio equal to 1/3. A layer of inert wire mesh (length 0.2 m) above the catalyst bed (length 0.5 m) was used in order to evaporate and preheat the feed. Extrudated zeolite BETA catalyst (diameter 3 mm, length 5 mm) was used in all experiments. The gas phase reaction was investigated in temperature interval 350-400 °C and pressure 3 MPa. The feed consisting of toluene and hydrorefined C9⁺ fraction from steam cracking unit mixture was tested too.

Computer Simulation

Computer simulations using ASPEN Plus[®] software were made to compare the experimental data with the simulation results.

Transalkylation



Isomerization

According to the literature [6] the equilibrium model including transalkylation (toluene + 1,2,4-TMB \rightarrow xylenes), disproportionation (TMB + toluene \rightarrow benzene + tetramethylbenzene) and isomeration (xylenes, TMB) was chosen to predict the studied system behaviour. The reaction conditions equal to those used in experiments were assumed. The reaction system being simplified as follows:

- Production of tetramethylbenzenes was limited only to the 1,2,4,5 – and 1,2,3,5-tetramethylbenzene isomers
 - Dealkylation of 1,2,4-TMB was supposed to yield toluene and ethene only, other possibilities being omitted
- Isomerization of both xylene and TMB isomers were taken into consideration.

Results and Discussion

Transalkylation tests

Application of non-refined C_9 fraction from steam cracking unit as a feed component in transalkylation led to fast catalyst deactivation and non-reproducible results. Performing model experiments with pure compounds turned to be a necessary step of the transalkylation study. Therefore the transalkylation of the equimolar mixture of 1,2,4-TMB and toluene was investigated in this study.

The experimental results measured at temperature 350 and 400 °C are illustrated in Figure 1. The dependence of conversion vs. kinetic coordinate W/F shows that only at higher temperature level 400 °C the chemical equilibrium was reached, because the main reaction components concentrations remained constant in a broad range of W/F. At lower temperature 350 °C the reaction rate was too slow to reach the chemical equilibrium. Therefore the system should be described in this study only by a pertinent kinetic model.

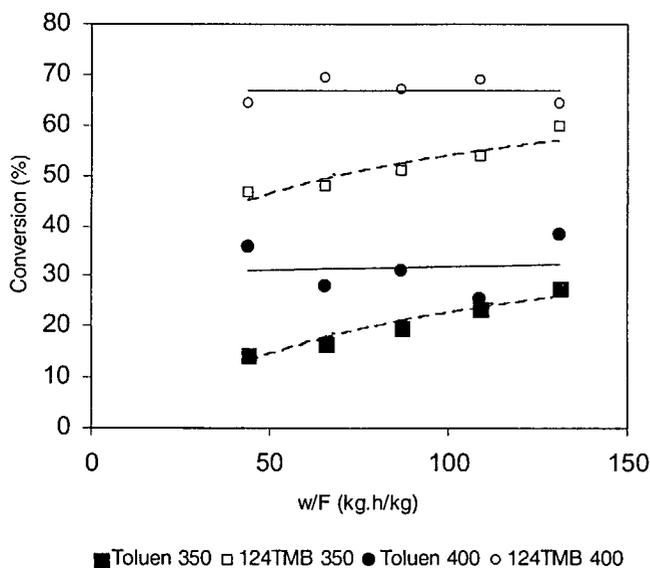


Figure 1. A plot of conversion vs. W/F parameter for equimolar feed of toluene and 1,2,4-trimethylbenzene, temperature 350°C and 400°C, respectively.

Table 1 brings the relation between the catalyst load and product concentration in more detail. Catalyst deactivation was also observed during the experiment as follows from the differences in the components concentrations at the same value of parameter W/F but at different times on stream during experi-

ment (compare the second and the last column of Table I). An equilibrium model was used to simulate the data measured at 400 °C. A comparison of experimental and simulation data is illustrated in Figure 2. Linear parity plot between the experimental and the simulation data was observed and the line slope was close to 1, indicating that proper chemical equilibrium model was chosen.

Table 1. The influence of catalyst load on the main components concentrations (wt. %). The experimental data at 400°C and 3.0 MPa

W/F (kg _{kat} h/kg) =	43.6	65.4	86.9	108.9	130.9	43.6
BENZEN	2.2	1.9	2.31	2.12	2.55	1.5
TOLUEN	23.6	25.19	31.06	29.66	32.03	28.88
m-XYLEN	19.52	19.257	17.9	17.48	17.17	16.07
p-XYLEN	9.04	9.03	8.55	8.34	8.2	7.78
o-XYLEN	8.59	8.46	7.78	7.68	7.48	7.15
135TMB	7.02	7.65	7.28	7.75	7.3	8.74
124TMB	16.95	18.4	17.18	18.39	17.28	20.76
123TMB	2.51	2.69	2.46	2.66	2.49	3.02
1245TEMB	1.79	1.91	1.43	1.53	1.38	1.75
1235TEMB	2.33	2.48	1.84	1.99	1.79	2.27

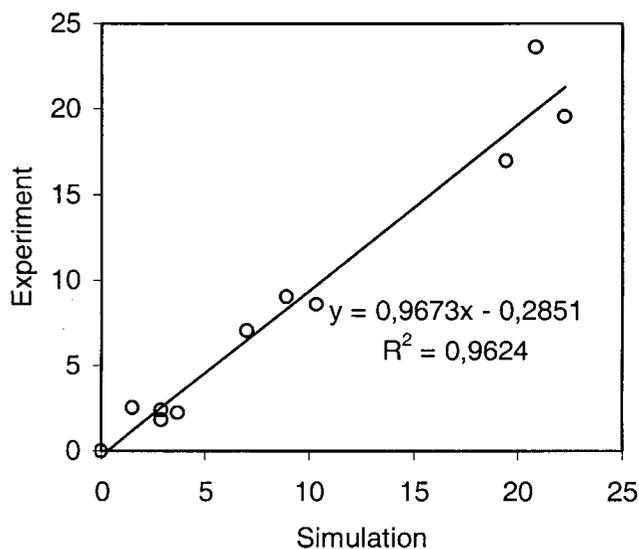


Figure 2. Simulation results and experiment data of reaction product concentrations (wt %) temperature 400°C and pressure 3.0 MPa

Process Simulation

An outlet stream of equilibrium reactor consists not only of key component, xylenes, but also of unconverted toluene, trimethylbenzenes and the other by-products – benzene, ethylene and tetramethylbenzenes. Therefore, this product mixture should be separated and purified. The set of rectification column was supposed, respecting the differences in boiling point

and volatility of aromatic hydrocarbons. The separation scheme by ASPEN PLUS™ was developed with the aim to withdraw the xylenes fraction as a distillate. The rectification set-up is documented in Figure 3, where four rectification columns are combined. The first column deals with the stripping of benzene and ethylene, the second one separates toluene and xylene together high boiling components and the third column was apply to purify the xylenes. The last column rectifies trimethylbenzenes out from tetramethylbenzenes and enables to reuse them in the feed. The product from the second (toluene) column is recycled back to the feed, too.

product and tetramethylbenzene bottom stream from column 4. The 6th column of the Table 3 summarises the composition of xylene stream, the concentration of the key component overcome 99 mass %. This stream could be further treat by isomeration or other method with the aim to concentrate one of the xylene isomers. The tetramethylbenzene stream is reach of the side products, tetraMB, which can be used for other purposes. There is a benzene stream consisting of approx. 33 % toluene, in total balance this looses represents 0,28 kg/h toluene, 6% from the total fed amount of toluene, see feed composition.

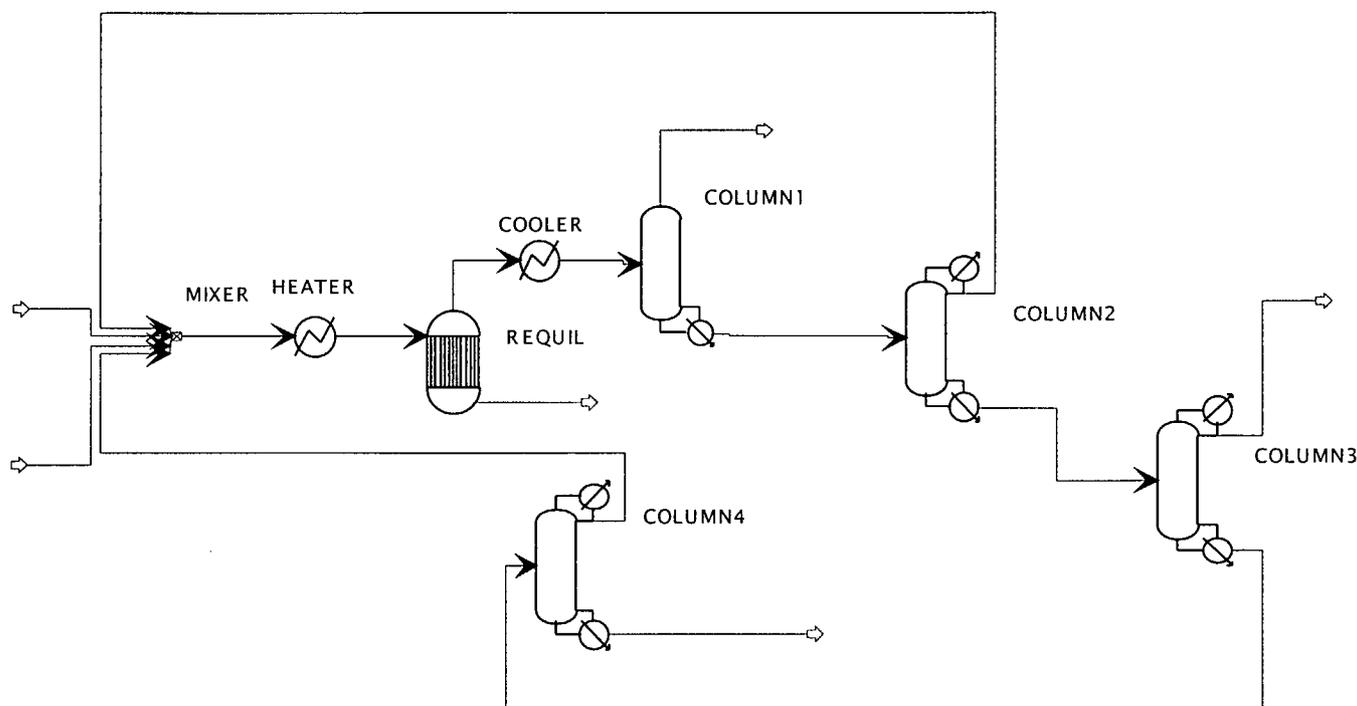


Figure 3. Schema of transalkylation unit consisting of equilibrium reactor and column system

Table 2. The column system for xylenes separation and purification by transalkylation of trimethylbenzenes and toluene

Column	Efficiency (theoretical stages)	Reflux ratio (mol)
COLUMN 1	7	-
COLUMN 2	40	4
COLUMN 3	20	4
COLUMN 4	20	2

The description of the separation system is given in Table 2 – the first column consist of only stripping section, light products (benzene, ethylene) are distilled out from the reaction mixture. The second, most important column separates toluene and xylene. The main task of rectification set-up is to fulfil mass and heat balance inside the system, if the recycles of trimethylbenzenes and toluene are applied. The results and corresponding temperature profiles are summarised in Table 3 and Figure 4.

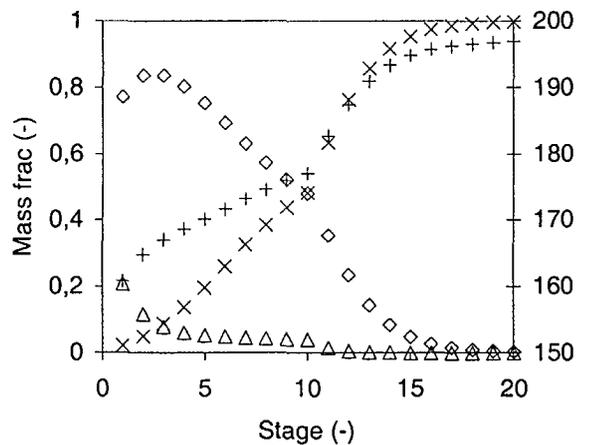
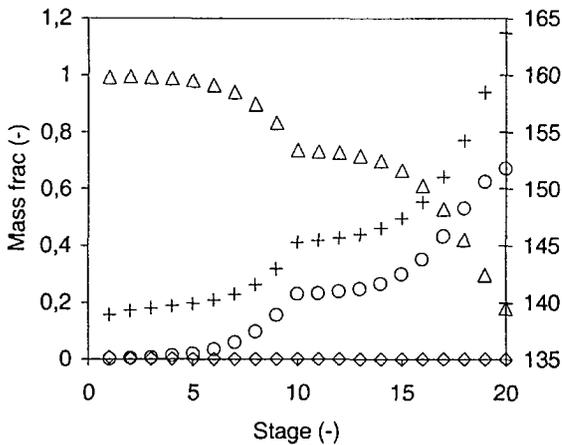
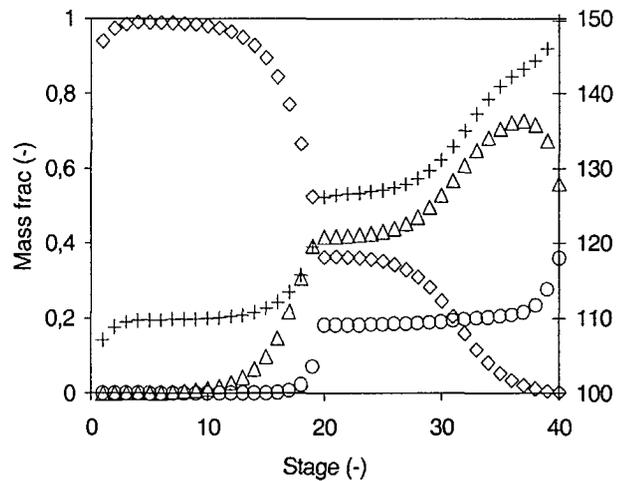
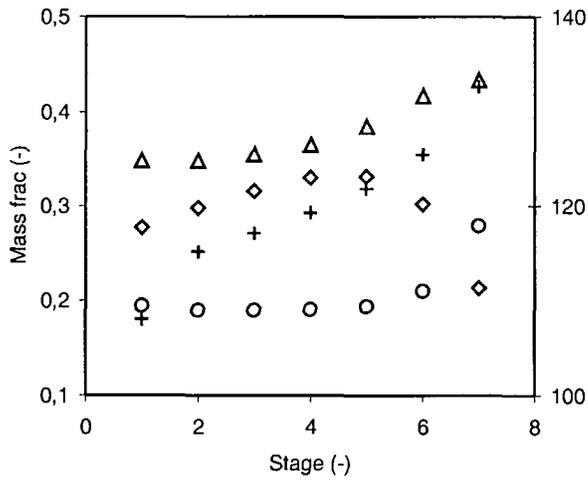
The results in Table 3 illustrate the distribution of the components in the outlet streams. There are only three product streams – benzene gas off from the column 1, main xylene

Conclusion

β zeolite has been proven to be a catalyst active and selective enough to catalyse transalkylation of trimethylbenzenes with toluene. As this catalyst is sufficiently active, reaction equilibrium can be reached at higher temperatures in a broad range of catalyst load with almost no compromise in selectivity. Relatively simple equilibrium model can be utilised to describe the system at higher temperatures and to scale up the reactor at these conditions. To describe the system at lower temperatures considerably below 400°C, utilization of a kinetic model seems

Table 3. The composition of Feed/Product streams from the xylene production

Mass Fraction	Feed	Reactor feed	Product	Benzene	Xylene	Tetramethyl-benzene
TOLUENE	0,4313	0,3929	0,223	0,33807	6,44E-03	8,52E-17
124TMB	0,5687	0,44009	0,181	0,02649	6,75E-04	1,52E-03
135TMB	0	0,06388	0,0650	0,01081	7,73E-04	1,43E-04
123TMB	0	0,01417	0,01435	1,68E-03	9,51E-06	9,37E-04
O-XYLENE	0	0,03712	0,1029	0,03545	0,18918	3,40E-07
M-XYLENE	0	0,02346	0,22178	0,10389	0,5711	5,36E-08
P-XYLENE	0	8,69E-03	0,08886	0,03776	0,23183	1,77E-08
1245TEMB	0	5,49E-03	0,03683	2,09E-03	9,19E-08	0,62942
1235TEMB	0	1,70E-03	0,01738	9,37E-04	3,03E-08	0,31514
1234TEMB	0	2,75E-05	2,65E-03	1,13E-04	7,72E-10	0,05285
BENZENE	0	0,01247	0,04198	0,38548	1,03E-10	0
ETHYLENE	0	0	4,38E-03	0,05722	0	0
Flow rate kg/hr	5,1	11,1	11,0999	0,85	3,70002	0,54986
Temperature C	20	90	400	108	138,9	196,9



◇ TOLUENE ○ TMB △ XYLENE + Temperature (°C)

◇ TMB △ XYLENE × TEMB + Temperature (°C)

Figure 4. Concentration (left x-axis) and temperature (°C, right x-axis) profiles along columns 1 to 4 for xylene separation

to be necessary. This kind of model would also make it possible to take catalyst deactivation into consideration.

Symbols

124TMB	1,2,4-trimethylbenzene
135TMB	1,3,5-trimethylbenzene
123TMB	1,2,3-trimethylbenzene
1245TEMB	1,2,4,5-tetramethylbenzene
1235TEMB	1,2,3,5-tetramethylbenzene
1234TEMB	1,2,3,4-tetramethylbenzene

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