

## PREPARATION OF TOLUENE FROM XYLENE

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The disproportionation of xylene to toluene has been studied in presence of different catalysts and catalyst concentrations.

**Key words:** Toluene, Xylene, Dealkylation.

### Introduction

Toluene is a strategic material and is an important intermediate for the synthesis of dyes and polymers. In view of its commercial significance, it was considered worthwhile to study its preparation from xylenes, which are now available in Pakistan.

There are numerous patents in the literature covering the manufacture of toluene from xylene [1-7]. The processes vary in the use of raw material, catalysts, temperature and pressure conditions.

During World War I, much attention was paid to the conversion of alkylbenzenes to toluene because of its non-availability in the desired quantity. Later on, studies were carried out for the possible commercial conversion of polymethyl benzenes to toluene by thermal cracking and by transfer of methyl groups to benzenes in presence of anhydrous aluminium chloride. The results of these studies were however not greatly encouraging. Boedther and Halse [8] found no toluene in the reaction of benzene with xylene in the presence of aluminium chloride at reflux temperature for 6 hrs. Fischer and Niggemann [9] obtained similar results. These investigators however reported that upto 12% toluene can be obtained from xylene at the reflux temperature in presence of 3-4% aluminium chloride. Egloff [10] described high temperature non-catalytic cracking process for solvent naphtha and claimed to have obtained 13-14% toluene. In this paper the reaction of alkyl aromatic hydrocarbons in the presence of various catalysts particularly those of the Friedel Crafts type have been described in some detail.

All the disproportionation reactions were carried out, except when mentioned otherwise, in the presence of a constant stream of anhydrous HCl gas.

### Materials and Methods

The usual GPR grade xylenes, except when specified otherwise, were used and dried over sodium wire. All of the catalysts were of the AR grade and were used as such.

The separation and analysis of the mixture obtained was done by a GO Mass Spectrometry under the following conditions:

Column length	2m.
Column material	OV101
Min. temperature	40°
Max. temperature	300°
Injector	100°
Detector	160°

### Programming.

IS01	IS02
2 min. 50°	1°/min. 5 min. 100°.

*Production of toluene in presence of anhydrous AlCl<sub>3</sub>.* A mixture of ortho-xylene (113.6 ml) and anhydrous AlCl<sub>3</sub> (4 gm) was refluxed for 5 hrs. The mixture was steam distilled to yield an oil which on distillation gave a fraction boiling between 80-200° leaving behind a tarry residue. The mixture of hydrocarbons obtained was separated and analysed to give 14% toluene (Table 1, expt. 1).

*Production of toluene in presence of anhydrous AlCl<sub>3</sub> and HCl gas.* A mixture of ortho-xylene (113.6 ml) and anhydrous AlCl<sub>3</sub> (4 gm) was refluxed for 5 hrs with constant passing of anhydrous HCl gas. The mixture was steam distilled to yield an oil and a tarry residue. The oil thus obtained was treated with Ca (OH)<sub>2</sub> to remove HCl and distilled to yield a fraction boiling between 80° and 203°. This fraction upon gas chromatographic analysis revealed that 15.2% toluene had been formed during the reaction alongwith 23.0% mesitylene and 6.45% other products while 55% xylene remained unchanged.

The experiment of disproportionation of xylene into toluene was repeated in a current of anhydrous HCl by varying the concentration of AlCl<sub>3</sub> and the results are given in Table 1.

*Production of toluene from commercial xylene.* A mixture of commercial xylene 4800 ml and anhydrous AlCl<sub>3</sub> (507gm) was refluxed under a current of anhydrous HCl for 5 hrs. The reaction mixture after steam distillation and removal of HCl from the oil layer by Ca (OH)<sub>2</sub> yielded a fraction which on analysis revealed the presence of 20.33% toluene.

*Production of toluene in presence of other catalysts.* A mixture of ortho-xylene 113.6 ml and anhydrous FeCl<sub>3</sub> (4gm) was heated under reflux for 5 hrs. The resulting mixture was



steam distilled to yield an oil which on analysis did not reveal the presence of toluene. The experiment was repeated with other catalysts such as  $\text{SbCl}_5$ ,  $\text{PbCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{MnCl}_2$  and  $\text{CuCl}_2$ . In all these cases no disproportionation of xylene into toluene was observed.

### Results and Discussion

A study was made of the products resulting from the de-alkylation of xylene under different variables. The latter were the catalyst and its concentration, reaction period and the presence or absence of a current of anhydrous HCl. When the reaction was carried out for 5 mins at reflux temperature with a 4%  $\text{AlCl}_3$  concentration, no conversion of xylene into toluene was observed. When the reaction time was increased successively for 5 mins to 5 hrs at the same catalyst concentration (4%  $\text{AlCl}_3$ ) the analysis revealed the presence of 14% toluene, 65.4% xylene, 10.3% mesitylene and 9.64% other products. These findings are an improvement on the study made by Fischer and Niggemann [9] who had obtained only a 12% yield of toluene.

When the de-alkylation reaction was carried out for 5 hrs in presence of a current of anhydrous HCl with the same catalyst concentration (4%  $\text{AlCl}_3$ ) there was a further increase in the yield of toluene which was recorded at 15.2%. The analysis also revealed 55% xylene, 23.3% mesitylene and 6.45% other products. The concentration of toluene in the reaction product increases successively with the increase in the catalyst concentration so much so that at 8%  $\text{AlCl}_3$  concentration the yield of toluene was 16.3% and at 12%  $\text{AlCl}_3$  concentration a 18.25% yield of toluene was obtained. However, when the concentration of anhydrous  $\text{AlCl}_3$  was increased to 20% no appreciable yield in toluene was obtained which remained constant at 18.12%, xylene 43%, mesitylene 25%, and other products 12.85%.

The experiment was repeated on a slightly larger scale

with 560 ml ortho-xylene to study the validity of the results with 12% anhydrous  $\text{AlCl}_3$  in a current of anhydrous HCl. The results were in accordance with the earlier findings and the analysis showed 18.07% toluene in the reaction product. These results illustrate that the best conversion of ortho-xylene into toluene was obtained by refluxing xylene for 5 hrs with 12%  $\text{AlCl}_3$  under a current of anhydrous HCl.

In an attempt to scale up the production of toluene and to adopt the reaction to more practical conditions the study was extended to the use of commercial xylene instead of pure ortho-xylene. In this case a production of 20.33% toluene, 40.5% xylene, 25.5% mesitylene and 13.12% other products was recorded when the reaction was carried out for 5 hrs with 4800 ml commercial xylene at a catalyst concentration of 12%  $\text{AlCl}_3$  in a current of anhydrous HCl. This is an important finding because the available literature only discusses the production of xylene from generally pure alkyl aromatic hydrocarbons and shows that the reaction is practicable and not restricted to pure ortho-xylene but can be carried out successfully with a commercial mixture of xylenes. The commercial xylene mixture had however, previously been analysed by GLC and was found to consist only of xylenes and was free from toluene. Another point of interest is that when commercial xylene was used an increased production of toluene (20%) was observed which is higher than that obtained with pure ortho-xylene.

The attempt of disproportionation of ortho-xylene into toluene in the presence of other catalysts however, did not meet with success. Several catalysts such as  $\text{FeCl}_3$ ,  $\text{SbCl}_5$ ,  $\text{SnCl}_4$ ,  $\text{PbCl}_2$  and  $\text{MnCl}_2$  were tried but in each case no conversion into toluene was obtained and the total xylene was recovered as such after a 5 hrs reaction period. This is however, in accordance with the findings in literature where no conversion of ortho-xylene into toluene has been obtained in presence of other transition metal catalysts.

TABLE 1. PREPARATION OF TOLUENE FROM XYLENE AT REFLUX TEMPERATURE IN PRESENCE OF DIFFERENT CATALYSTS AND HCl GAS.

Exp. No.	O-xylene	Catalyst	% age of catalyst	Time	Yield%			
					Toluene	Xylene	Mesitylene	Other products
1.	113.5 ml	$\text{AlCl}_3$	4	5 hrs.	15.2	55.0	23.3	6.5
2.	113.6 ml	"	8	5 "	16.3	45.5	27.8	11.0
3*	113.6 ml	"	4	" "	14.0	65.4	10.8	9.6
4.	113.6 ml	"	4	5 mins.	Total xylene recovered			
5.	114.6 ml	"	12	5 hrs.	18.3	45	24	11.2
6.	113.6 ml	"	16	" "	15.5	46.9	6.4	10.7
7.	113.6 ml	"	20	" "	18.1	43	25.8	12.9
8.	568.0 ml	"	12	" "	18.1	45.9	22.1	12.6
9.	4800.0 ml (Commercial xylene).	"	12	" "	20.3	40.5	25.5	13.1

\*Exp. No. 3 was done in the absence of HCl gas.

### Conclusion

The foregoing discussion reveals that xylene can be converted into toluene under practical conditions of temperature and pressure. This has a definite advantage over the gas phase transformation of xylene into toluene where higher temperature and a sophisticated plant is required. The conversion of xylene into toluene under a current of HCl in presence of anhydrous AlCl<sub>3</sub> can be carried out, when required at a small and medium industrial scale suited to our conditions, quite conveniently, without the use of large scale plants and instruments when toluene is not available from the conventional sources. The xylenes obtained at the end of the reaction can be recycled while mesitylene can be converted into toluic or benzoic acid after oxidation and ultimately could lead to toluene. It can also be nitrated to give an intermediate used in the synthesis of vit. E.

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