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# **Dealkylation of Organic Compounds**

## Benzene from Toluene

## This catalytic dealkylation process which forms benzene from toluene in high yields is applicable to other organic compounds, including naphthalene from methylnaphthalene-containing feeds

 $\mathbf{L}_{N}$  BOTH straight-run petroleum distillates and refinery-processed fractions, high purity toluene is considerably more abundant than benzene. Dealkylation of toluene may be necessary where benzene is in short supply, as where a manufacturer has insufficient benzene, but excessive toluene production. If a satisfactory process could be developed for this most difficult dealkylation, it should be of wide application to other com-

# Table I. Demethylation of AromaticHydrocarbons Has Been Studied

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Supject	reference
Noncatalytic kinetics of toluene	(001)
Thermal dealkylation of high	(0, 24)
m.w. hydrocarbons with H <sub>2</sub>	(2, 18)
Concurrent dealkylation of	
aromatics and dehydrogena-	(10.00)
tion of naphthenes	(19, 23)
Alone catalysts with $H_{a}$	(15)
Demethylation of methyl-sub-	(10)
stituted benzenes using MoO <sub>3</sub> -	
Al <sub>2</sub> O <sub>3</sub> or Cr <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> catalysts	
with H <sub>2</sub>	(8, 10)
Dealkylation of hydrocarbons by	
groups of and 8 metal oxides	(11)
Dealkylation of aromatic hydro-	(14)
carbons by FeCl <sub>2</sub> catalyst with	
H <sub>2</sub>	(5)
Dealkylation of monocyclic	
aromatic hydrocarbons by	
AlPO <sub>4</sub> with $H_2$	(6)
ing Ni on distomaceous earth	
with H <sub>2</sub>	(20)
Demethylation of methylnaph-	
thalenes	
Using NiO-Cr <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> with	
	(9)
Using Ni or Co on silica gel	(17)
Dealkylation of high m.w. hydro-	(17)
carbons using alkali-promoted	
$Fe_2O_3$ , $Cr_2O_3$ with $H_2 + H_2O$	(1)
Toluene to benzene by methyl-	
group transfer with acid	(10)
Catalysis Disproportion of toluono	(16)
Over aluminosilicate catalysts	(21)
Using cracking catalysts with	(~~~)
H <sub>2</sub>	(4)
Demethylation of methyl-sub-	
stituted aromatics using SiO <sub>2</sub> -	
Al <sub>2</sub> O <sub>3</sub> cracking catalysts with	IN 11 10
$\mathbf{n}_2$	(1, 11-13)

pounds, including production of dealkylated fused ring compounds such as naphthalene from alkylated naphthalene feeds. This has been found to be the case.

Few published data relating to the conversion of toluene to benzene have appeared. Most of the processes deal with dealkylation of aromatic hydrocarbons containing at least two carbon atoms in the alkyl side chain. This reaction proceeds readily and in good yields, whereas it is difficult to remove the methyl group. Essentially three types of toluene-to-benzene processes have been considered: (1) disproportionation of toluene to benzene and xylenes; (2) hydrogenolysis (hydrocracking) of toluene to benzene and methane; and (3) methyl group transfer reactions (Table I).

This article deals with the hydrogenolysis or hydrocracking process for transforming toluene to benzene on a pilot-plant scale.

### Thermodynamics

The principal reaction studied is:

 $C_6H_5CH_2 + H_2 \rightarrow C_6H_6 + CH_4 \quad (1)$ 

In Table II, data are also given for the following side reactions which occur under certain conditions:

- $C_6H_5CH_3 + 3H_2 \leftrightarrows C_6H_{11}CH_3 \qquad (2)$
- $C_6H_5CH_3 + 10H_2 \rightarrow 7CH_4 \qquad (3)$

Equations 2 and 3 are favored by high hydrogen partial pressures and lower temperatures. Both reactions are far more exothermic than the desired reaction (Equation 1). Reactions 1 and 3 are irreversible in the temperature range studied. Diphenyls may be formed by dehydrogenation:

$$2C_{6}H_{5}CH_{3} \leftrightarrows CH_{3}C_{6}H_{4} -$$

$$C_6H_4CH_3 + H_2 \quad (4)$$

$$2C_{6}H_{6} \leftrightarrows C_{6}H_{5} - C_{6}H_{5} + H_{2} \qquad (5)$$

$$C_{6}H_{6} + C_{6}H_{5}CH_{3} \rightleftharpoons C_{6}H_{5} - C_{6}H_{4}CH_{3} + H_{2} \quad (6)$$



Figure 1. Using two stainless steel tubes in the reactor section saved time in regenerating and studying various hydrogenolysis catalysts

				Heats of Reaction					
Equilibrium Constants, K		Gram Cal./Gram Mole			B.t.u./Lb. Mole				
Temp., ° K.	Eq. 1	Eq. 2	Eq. 3	Eq. 1	Eq. 2	Eq. 3	Eq. 1	Eq. 2	Eq. 3
700 800 900 1000	1473 522 228 116	$\begin{array}{c} 2.97 \times 10^{-5} \\ 2.91 \times 10^{-7} \\ 8.06 \times 10^{-9} \\ 4.64 \times 10^{-10} \end{array}$	$egin{array}{c} 8.66  imes 10^{24} \ 1.13  imes 10^{18} \ 2.51  imes 10^{13} \ 4.25  imes 10^9 \end{array}$	- 12,500 - 12,900 - 13,300 - 13,600	-51,600 -51,500 -51,200 -50,800	-135,700 -139,400 -142,300 -144,500	-22,500 -23,300 -23,900 -24,300	- 93,000 - 92,800 - 92,300 - 91,500	-245,000 -251,000 -256,000 -260,000

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## Apparatus

The reactor section consists of two stainless steel pipes (Type 316, schedule 40) 1.25 inches in diameter and 50 inches long, with a similar 0.25-inch pipe as thermocouple well throughout the length of each reactor (Figure 1). Using two tubes saved considerable time in regenerating and studying various catalysts alternatively. With the rubber O-ring type closure, a knurled nut at the bottom of each reactor could be tightened by hand for sealing. A jacket equipped with inlet and outlet for cold running water surrounded each O-ring, preventing burn-out at the processing temperatures used. Each reactor is surrounded by the molten-lead bath, agitated by an impeller-stirrer driven by an air motor. The temperature of the bath is controlled by a Leeds & Northrup Micromax controller. Six thermocouples are placed in each reactor; five are equally spaced throughout the catalyst zone,

and one, the bottom of the quartzpacked preheater section, indicates temperature of the feed before it touches the catalyst. The toluene is fed into the reactor by a Hills-McCanna duplex pump, which also introduces steam into the reactor as liquid water except at rates of 50 ml. per hour and less. For these low rates, a positive displacement pump was designed, which could deliver as little as 1 ml. of water per hour.

## **Materials**

The benzene was thiophene-free reagent grade, and toluene was nitration grade. Steam, introduced into the reactor as distilled water, was pumped into the preheat section of the reactor, where vaporization occurred.

Catalysts were prepared by impregnation of an activated alumina with aqueous solutions of salts. This activated alumina had been pelleted and calcined at 600° C. for 4 hours before

Figure 2. More

steam is required

at higher temperatures for com-

parably high C<sub>6</sub>H<sub>6</sub>

selectivity

impregnation. The reagent grade chemicals used were cobaltous nitrate, ammonium molybdate, chloroplatinic acid, and sodium hydroxide. Except for the platinum-containing catalyst, all were recalcined at  $600^{\circ}$  C. for 6 hours after impregnation and drying at 100° C. The platinum-containing catalyst was dried at 100° C. and brought to reaction temperature of 566° C. by placing it in the heated reactor.

## Method of Analysis

The benzene and toluene content of the liquid products was obtained by first distilling off the benzene-toluene cut from the heavy ends. Two methods were used for determining the benzene content of the overhead product-i.e., ultraviolet absorption spectra, and comparison of liquid boiling points with that of known mixtures of benzene and toluene in the same Cottrell ebulliometer (25). Besides being more rapid, the latter appeared to be more accurate. Apparently, small quantities of impurities in the benzene-toluene overhead product adversely affected the ultraviolet spectra. Only under conditions where ring hydrogenation occurred were sufficient naphthenes formed to affect the boiling point method of analysis.

#### Table III. Catalysts Containing Molyb-Are Best under Reaction dic Acid **Conditions Used**

 $(1050^{\circ} F.; 30 p.s.i., 1.0 LHSV hour^{-1};$  $3.4 H_2/C_7H_8$  mole ratio)

$Catalyst^a$	Hydro- carbon Re- covery, Vol. % <sup>b</sup>	C₅H̃₅ in Product, Mole %
0.5% platinum <sup>e</sup>	92	2.5
3% cobaltous oxide <sup>c</sup>	97	1.5
8.7% molybdenum tri-		
oxide	91	8.5
Cobalt molybdate <sup>d</sup>	91	9.5
+0.5% sodium hy- droxide +0.2% sodium hy-	93	10.7
droxide	9 <b>0</b>	14.3
droxide	9 <b>0</b>	14.3

 $a_{1/8} \times \frac{1}{8}$  inch pellets; alumina was vdrous form stabilized with silica. <sup>b</sup> Norhydrous form stabilized with silica. mally liquid hydrocarbons. <sup>o</sup> In hydrous Al<sub>2</sub>O<sub>3</sub> stabilized with silica. <sup>d</sup> Cobalt molyb-° In hydrous date-alumina-type catalyst.



## **Comparison of Some Catalysts**

A series of catalysts was compared (Table III) using identical processing conditions. The liquid hourly space velocity was calculated as the volumes of liquid toluene at 25° C. fed through the reactor per volume of catalyst per hour. It is apparent that catalysts containing molybdic acid are best under the reaction conditions employed.

Most of the experimental work was carried out using a cobalt molybdate catalyst without alkali treatment.

## **Effect of Operating Conditions**

Steam Partial Pressure. For toluene conversions per pass of 25% and higher, superatmospheric pressures were necessary. Under these conditions, in the absence of steam, a highly exothermic reaction occurs, transforming a considerable amount of the feed to methane. This deleterious reaction, which occurs according to Equation 3, is largely localized at the entrance end of the catalyst zone. When steam was introduced into the reaction zone during passage of the toluene and hydrogen, this hydrocracking reaction could be entirely suppressed. At a fixed temperature and pressure, and with a given hydrogentoluene mole ratio, there is a critical minimum amount of water vapor which

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must be used for any given throughput rate. In general, the higher the hydrogen-toluene mole ratio, or the higher the total operating pressure, the larger the amount of steam required (Figure 2).

It is not known how steam functions in suppressing this deleterious hydrocracking reaction of the feed to methane. It may place the catalyst in a different oxidation state, which renders it less active for hydrocracking the toluene to methane. Probably the most active centers of the catalyst are the most strongly adsorbing and, consequently, in the absence of steam cause most of the hydrocracking. In the presence of controlled amounts of steam, these strongly adsorbing centers would be expected to be effectively poisoned. This poisoning effect is temporary, as pronounced hydrocracking is soon exhibited when steam is temporarily stopped. The effectiveness of steam in suppressing hydrocracking appears specific; neither methane nor nitrogen appeared nearly as effective. This indicates that decreasing the hydrogen partial pressure is not the only effect of steam introduction. A more specific explanation might be reduction in acidity (and hence cracking activity) of the catalyst. Thus, the effect of steam and of alkali in suppressing deleterious hydrocracking of toluene might be similar.

The optimum amount of steam to be

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used in this hydrogenolysis reaction has not been accurately determined. If the catalyst is to maintain its activity for long periods without regeneration, it will probably be necessary to use not less than an experimentally determined lower limit, generally greater than 0.5 mole of steam per mole of toluene. This amount should help eliminate the deposition of carbonaceous matter on the catalyst from cracking of the feed and products besides eliminating hydrocracking of the feed to methane.

**Reaction Pressure.** From Equation 1, it might not be expected that increased pressures would cause significantly higher conversions, as there is no volume decrease in the formation of the reaction products from the reactants. Actually increased pressures cause higher conversions at the same contact time and under identical hydrogen-toluene and steam-toluene molecular ratios (Figure 3). This may be due to increased activities caused by a preferential adsorption of the reactants, with consequent decreased adsorption of steam.

At the highest pressures studied, 1500 p.s.i. at  $1050^{\circ}$  F., there is some hydrogenation of the toluene to naphthenes, probably dimethylcyclopentanes and methylcyclohexane. With a lower hydrogen partial pressure or increased reaction temperature; this side reaction can be eliminated at the same operating pressure.

Increased pressures have a definite beneficial effect in giving higher over-all





Figure 4. Increase in reaction temperature markedly increases reaction rate

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Figure 5. Remarkably pure benzene is produced by a continuous process

yields of benzene. Thus, increasing the pressure from 250 to 1000 p.s.i. increases yield from 83 to over 97 mole %.

Reaction Temperature. Increase in reaction temperature has a marked influence on reaction rate (Figure 4). At a reaction pressure of 1000 p.s.i. with a steam-toluene mole ratio of 2.94 to 1.0, the reaction rate is doubled for 100° F. increase in temperature. For these reaction conditions, the mole ratio of hydrogen to toluene was 1.90 to 1.00. Under the same conditions with a hydrogen-toluene mole ratio of 3.85 to 1.00, the reaction rate is doubled with a temperature increase of only 70° F., even though contact time is only two thirds as long.

Alkalies in Catalysts. Incorporation of a small amount of sodium hydroxide in the cobalt molybdate catalyst enhanced its activity for methyl group removal (Table III) at 1050° F. and 30 p.s.i. without added steam. In the presence of added steam at 1000 instead of 30 p.s.i. cobalt molybdate catalyst containing 0.2% sodium hydroxide gave a slightly lesser conversion to benzene per pass than the alkali-free catalyst; however, yield of benzene was essentially quantitative (Table IV).

Table IV. Addition of Alkali Gives Essentially Quantitative Yield

	Without NaOH	With 0.2% NaOH
Temperature, ° F.	1051	1050
Pressure, p.s.i.	1000	1000
LHSV for toluene,		
hour <sup>-1</sup>	1.0	1.0
Mole ratios		
$H_2/C_7H_8$	3.71	3.81
$H_2O/C_7H_8$	1.41	1.40
Hydrocarbon re-		
covery, vol. %	93.8	95.8
Conversion to ben-		
zene, mole %	38.9	35.4
Benzene selectivity,		
mole %	95.1	99.8

## **Recovery of Pure Benzene**

The benzene produced from toluene by this process is remarkably pure. Any compounds or unstable impurities in the original toluene are essentially decomposed or transformed into products which are not present in the benzene fraction. A flow diagram for the continuous production of benzene from toluene is given in Figure 5. The feed consisting of toluene, steam, and hydrogen is heat exchanged with the reaction products. Additional heat as required to raise the feed to the reaction temperature is supplied by a small preheater. The gaseous product (make gas) is separated from the water and liquid hydrocarbons and the latter are fractionated in three distillation columns to produce a light ends fraction, benzene, toluene, and heavy ends fraction. The toluene is recycled with make-up toluene to the dealkylation unit.

## Application of Process to Other Compounds

This process may be applied to the removal of one or more alkyl groups from a wide variety of organic compounds, depending on processing conditions. Besides alkylated benzenes, fused aromatics such as alkylated naphthalenes, methylnaphthalenes, and polymethylnaphthalenes may be dealkylated. The optimum processing conditions for various organic compounds are substantially different from those used to make benzene from toluene.

### Conclusions

Toluene has been converted in 95 mole % yield to benzene by catalytic reaction with hydrogen in the presence of steam. Thirty to 50 mole % conversion is obtained per pass at 1050° to 1100° F., 1000 p.s.i., with a toluene liquid hourly space velocity of 1.

A cobalt molybdate catalyst is effec-

tive for this conversion. A small amount of alkali incorporated in this catalyst results in an essentially quantitative yield of benzene from toluene by reaction with hydrogen in the presence of steam, which eliminates deleterious hydrocracking of the toluene to methane.

This process is applicable to the dealkylation by hydrogenolysis of a wide variety of organic compounds, including naphthalene from methylnaphthalenecontaining feeds.

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