

### XII. SYNTHESIS OF TOLUENE FROM BENZENE AND METHANOL

#### Introduction:

The process for synthesis of toluene by reaction of an excess of Benzene with Methanol at medium pressure over an acid zinc silico-phosphate catalyst was originally developed at Leuna. A commercial plant with a design capacity of 5,000 T/month of Toluene was erected at Waldenberg in Silesia where the I.G. have a factory which includes a Methanol plant. O.U.D.A. erected the plant, W.I.F.O. financed it and it was operated by the I.G. on a management-fee basis.

The Waldenberg plant started operations in mid-1942. The maximum achieved production was 3,800 T/month of Toluene but latterly only 2,500-3,000 T/month were made on account of transport difficulties and consequent shortage of raw materials.

A description of the process and of the Waldenberg plant was provided in the first place at Leuna by Dr. Herold, the head of the Development Department. His information was later confirmed and some additional data produced, also at Leuna, by Dr. Klopfer who was in charge of catalyst testing. A process description was also found in an I.G./W.I.F.O. Agreement, a copy of which was removed from Leuna.

#### General Process Data:

Methanol and Benzene used for the process must be as free as possible from impurities, particularly nitrogen compounds. Methanol is specially purified from amines, by means of an organic cation exchanger, down to a maximum nitrogen content equivalent to 2 mgms  $\text{NH}_3$ /litre. Nitriles are the chief impurities in the benzene and no satisfactory method has been developed for their removal; formation of zinc chloride addition compounds not successful. In the end, the I.G. have resorted to careful analytical control of all batches of benzene so that these can be blended to give a feed to the plant which never contains more than 0.5 mgms  $\text{NH}_3$ /litre.

Benzene and Methanol are reacted in the molecular ratio 4:1. Reaction temperature is 340-380°C and pressure 30-35 ats. Feed rate is 0.25  $\text{M}^3/\text{M}^3$  catalyst volume/hour with fresh catalyst. In order to maintain the catalyst in an active form steam must be added to the reactants. Substantially all the Methanol is converted in a single pass.

The catalyst, which has a life of 4-6 weeks, was stated by Dr. Klopfer to have the following composition:-

ZnO	6%
P <sub>2</sub> O <sub>5</sub>	60%
Kieselguhr	25%
Acid treated Bleaching Earth	8%
Water	4%

Dr. Hanish stated that the catalyst was made by mixing ortho-phosphoric acid, Kieselguhr and zinc oxide, and drying a 2 cm deep layer of the resultant paste at a temperature below 250°C. The cake obtained is broken up and sieved, pieces of about 20 mm size being used as catalyst. Fine material, amounting to about 30% of the charge, is recycled to the pasting stage.

Loss of activity of the catalyst is caused by carbon formation during reaction; after 4 - 6 weeks the catalyst contains about 4.0% carbon. Attempts to revivify catalyst by burning off this carbon were unsuccessful because of conversion of ortho-phosphoric into the inactive metaphosphoric acid.

#### Plant Operation:

The Waldenberg plant consisted of 14 units, each consisting of 1 converter 1700 mm. external diameter and 16 M long. Each converter contained 15 M<sup>3</sup> of catalyst. FIGURE VIII shows the general layout of a unit. Benzene and Methanol in the weight ratio 9:1 are injected at 35 ats and pass through a heat exchanger and gas-fired preheater where they are vaporised and heated to 280°C (Dr. Klopfer) or 350°C (Dr. Harold). They then enter the top of the reaction vessel which is divided into four or five catalyst beds separated by layers of Raschig rings. Cold benzol is injected in controlled quantity at the entry to the converter and to each of the Raschig ring beds in order to maintain a reaction temperature of about 370°C with a maximum of 380°C. The reaction is extremely exothermic, the heat evolution per converter being 100,000 Kg. cal./hour. There is a layer of calcined lime about 90 cms. thick at both the top and bottom of each converter. Lining of the converter is acid-resistant refractory brick. A 5% caustic soda solution is injected into the products immediately on leaving the converter in order to prevent corrosion by phosphoric esters. The products then pass via the interchanger and a water-cooled condenser to a separator vessel. Gas, consisting of methane, CO<sub>2</sub>, CO dimethylether and benzene vapour, is removed from the top of this vessel and is compressed and cooled to recover benzol (800 grms/M<sup>3</sup>). The liquid product separates into water and hydrocarbon layers, the latter having the average composition:

71 -	80%	vol.	Benzene
12 -	17%	"	Toluene
4 -	6%	"	Xylene
4 -	6%	"	Higher methyl benzenes.

The production of 1 Ton Toluene requires 1.45 T Benzene and 0.85 T. Methanol.

The water layer is distilled for recovery of a small amount of unreacted Methanol which is returned to feed. The hydrocarbon product is first fractionated (2 packed columns of 1100 mm. diam.) to remove benzol and dimethylether as overheads. The bottoms pass to a second distillation stage (3 packed columns also of 1100 mm. diam) in which most of the benzol and only a trace of Toluene is distilled over. The next distillation is for complete stripping of Benzene from the product. This is carried out in 3 60 plate columns of 2,400 mm. diameter and the overhead contains some 15% Toluene. These overheads are returned to the feed of the first benzene-removal column.

The benzene-free bottoms of the third distillation stage are next fed to two 3,000 mm. diam. 60 plate stills from which a nitration grade Toluene is taken overhead. The fifth stage of distillation consists of the separation of the fourth stage bottoms into Xylene and heavier alkyl benzenes.

Development work on Related Processes:

Leuna have experimented with the reaction of Benzene with alcohols containing upwards of 5 carbon atoms, available as by-products of the higher alcohols synthesis. The same catalyst and general conditions as used for Toluene synthesis have been employed.

Long chain alkylates are not formed. Instead, splitting of the alcohol occurs giving simpler alkyl benzenes and some olefines which can be recycled.

Isopropyl benzene was the main product obtained. The above experiments reached the semitechnical stage and a large-scale plant was being considered for Heydebrech.