XXI. 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. 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 is 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. 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 M^3/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_2O_5	60%
Kieselguhr	25%
Acid treated Bleaching Earth	3%
Water	6%

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

Loss of activity of the catalyst is caused by carbon formation dur reaction; after 4-6 weeks the catalyst contains about 40% carbon. Atte to revivify catalyst by burning off this carbon were unsuccessful becau of conversion of orthophosphoric 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 contain 15 M^3 of catalyst. Fig. XXXVIII 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. Herold). They then enter the top of the reaction vessel which is divided into four or five cataly 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. cals/hour. There is a layer of calcined lime about 80 cms. thick at both the top and bottom of each convert 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 separato vessel. Gas, consisting of methane, CO_2, CO dimethylether and benzene vapour, is removed from the top of this vessel and is compressed and cooled to recover benzol (800 grms/M^3). The liquid product separates into water and hydrocarbon layers, the latter having the average composition:

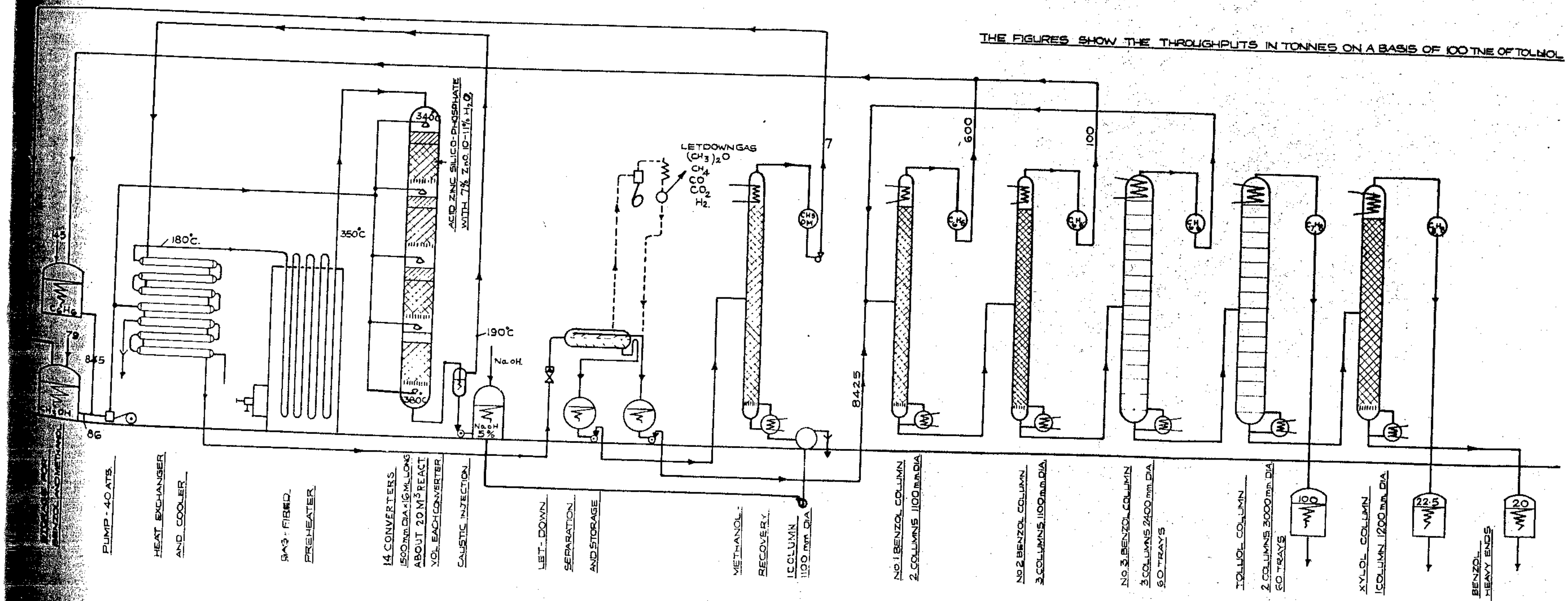
71 - 80%	vol.	Benzene
12 - 17%	"	Toluene
4 - 6%	"	Xylene
4 - 6%	"	Higher methyl benzenes.

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 to 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.

FIGURE XXXVIII

TOLUOL SYNTHESIS - CAPACITY 5000 TNE/MONTH - WALDENBURG - SCHLESIEN.



THE FIGURES SHOW THE THROUGHPUTS IN TONNES ON A BASIS OF 100 TNE OF TOLUOL

The benzene-free bottoms of the third distillation stage are next fed to two 3,000 mm. diameter 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.

XXII. CATALYST PREPARATION

The compositions and method of preparations were obtained for all catalysts that had been manufactured or used at Leuna for the preparation of fuels, oils, etc. Since many of the senior officials had left the district, most of the personnel interrogated were of the second or lower ratings, and were not familiar with all the details of the processes in question. In particular, Dr. Emil Schich had replaced Dr. S. Schneider as Works Manager. In addition, the time available, before the Russians moved into the area, was insufficient for a thorough analysis of the methods of manufacture of catalysts and there was no opportunity to make a study of the catalyst plant and its equipment. It is believe, however, that the information on composition and preparation of catalysts is adequate and that the catalysts could be prepared after only the usual amount of experimentation. The information on the methods of manufacture was obtained from Dr. Kurt Hill.

Purchase of chemicals for catalyst manufacture was not made on the basis of specifications, as is the general rule. The principal metal oxides and salts were purchased by "mark", and were in all instances the technically pure grade. Distilled water or condensate was used throughout for making solutions and for washing. Condensate was usually freed from oil by use of a charcoal filter.

The numbering of catalysts at Leuna has not been systematic; the only certain information conveyed by the numbering is the chronological order in which they were produced commercially. For the principal catalysts, estimated productions at the peak of manufacture have been given.

Catalyst 616

Use: Methanol synthesis, from carbon monoxide and hydrogen.

Composition:	Cr_2O_3	33%
	ZnO	60%
	Graphite	1%
	Water and impurities	6%

Preparation: Sixty kilograms of chromic acid anhydride is run in a chaser for thirty minutes; 100 kg. of zinc white is added and the mixing continued for 20 minutes. Thirty litres of water is next added, and ten minutes later 1 kg. of graphite (natural). Mixing is continued until all components are well blended. The chaser is then emptied, the charge is passed through a drum sifter (coarse pieces are returned to the chaser), and the mixture is pressed into 9 mm. pellets.

Quantity: 30 tons per month.

Catalyst 1132

Use; Isobutanol synthesis, from carbon monoxide and hydrogen.

Composition:

Cr_2O_3	33%
ZnO	60%
Graphite (natural)	1%
K_2O	1%
Water and impurities	5%

Preparation; Procedure is the same as for catalyst 616, except that O is introduced by adding potassium hydroxide or potassium carbonate along with the zinc white, Good mixing and fine grinding are again important factors.

Quantity: 60 tons per month.

Samples: Nos, 17 and 18.

Catalyst 1750 A mild hydrogenation catalyst.

Use: After-hydrogenation of higher alcohols (same as No. 1930).

Composition:

Cu	1.25 mol.
Cr_2O_3	0.50
ZnO	1.00

Preparation: 125 kgs, of copper sulphate ($CuSO_4.5H_2O$) is dissolved in 0 litres of water. 50 kgs. of Chromic acid anhydride is dissolved in litres of water and reduced with SO_2. After mixing the two solutions, solution of 200 kg, of sodium carbonate in 500 litres of water is added constant stirring, When the precipitation is finished, 15.1 kg. of white is added while stirring. The whole is heated to 78° C and held this temperature for 24 hours (alcohol bath). The contents are withdrawn into a filter, washed, dried and pressed into pellets.

The time spent in mixing, heating, etc., was said not to be critical.

Sample: No. 73.

Catalyst 2493

Use: Dehydrogenation of alcohols to aldehydes.

Composition:

ZnS	25%
Pumice (Italian)	75%

Preparation: The pumice is broken into 4-7 mm. granules, sifted and washed. Ten kg. of wet pumice is run in a pill-coating apparatus until the pieces are uniformly coated with the 3 kg. of zinc sulphide (Merck) that is added. The grains are put in shallow metal pans, dried for 12 hours at 80-90°C and sifted to remove fines.

(Not made for last 4 years.)

Catalyst 2730

Use: Polymerisation of isobutylene to iso-octylene (used for relati pure isobutylene).

Composition:

H_3PO_4	35%
Activated carbon	60%
Water	5%

Preparation: Eight kgs. of activated carbon, 4 litres of water and 5.12 kg. of phosphoric acid are run in the mixer until all the liquid is absorbed. The mass is then dried for 24 hours at 80-100°C.

Catalyst 3076

Use: Hydrogenation of di-isobutylene to iso-octane. Also hydrogenation of Kogasin.

Composition:

NiS	2 mols.
WS_2	1 mol.

Preparation: Fifty kgs. of nickel powder is dissolved in 250 litres of 60% HNO_3. The nickel is then precipitated by adding a solution containing 90 kg. of sodium carbonate (volume said not be be highly important). The precipitate is filtered, washed free from nitrate and dried. The dried material is ground and analysed. For each 25 kg. of nickel found by analysis there is added to the metal precipitate in a kettle, 50 kg. of $WO_3.H_2O$ in 25 litres of water. The contents are mixed continuously and evaporated to a thick paste. The mass is then put into shallow metal pans, dried for 12 hours, recovered from the pans, treated at 400° C. with H_2S, ground, mixed with 1% of graphite and pelleted. These pellets are ground and reformed into 10 mm. pellets.

Quantity: 1 ton per month.

Sample: No. 9.

Catalyst 3390

Use: Strong hydrogenation catalyst, for example, hydrogenation of phenol to cyclohexanol.

Composition:

Ni	3 mols
Al_2O_3	1 mol

Preparation: Nickel powder (70.6 kg.) is dissolved in the stoichiometric amount of strong nitric acid in a small agitator: 21.56 kg. of sheet aluminum is dissolved in a second small agitator with caustic soda solution (stoichiometric quantity of NaOH, concentration not important). The small agitators are then filled up with water, and the two solutions simultaneously run into a large agitator which originally contains about 1 M3 of water. The filling operation takes about half an hour, but time is not critical. Caustic soda solution is added for precipitation. The precipitate is separated in a filter press and washed well with water. The filter cake is removed and dried for about 8 hours at 200° C. in a drying oven, then ground and pressed into 5 mm. pellets.

Quantity: 1 ton per month.

Sample: No. 70.

Catalyst 3510 (Not made since 1935/1936; replaced by catalyst 5058).

Use: Vapour phase hydrogenation of middle oil to gasoline.

Composition:

MoO_3	1 mol
ZnO	1 mol
MgO	1 mol

Preparation: The three materials are pasted with water, spread on a metal plate, cut into cubes and dried.

Catalyst 4577

Use: Preparation of stearylamine from stearic acid and methylamine.

Composition:

NiS	1 mol
MoS_2	1 mol

Preparation: Two solutions are prepared separately:

(a) 45.36 kg. molybdic acid anhydride (MoO_3) in 100 litres of 50% caustic soda, and
(b) 91.67 kg. nickel nitrate ($Ni(NO_3)_2.6H_2O$) in 100 litres of water. solutions are run simultaneously and slowly (24 hours) into an agitator. precipitate is removed and washed on a filter press. The filter cake then dried at 100° C. and is formed into tablets in a hydraulic press. tablets are broken by hand into 4-6 mm. granules and converted into sulphide as described above under catalyst 3076.

(Note: There is a large loss of MoO_3 due to incomplete precipitation).

<u>Quantity</u>: 100 kgs. per year.

Catalyst 4788

<u>Use</u>: Hydrogenation of acetylene to ethylene (ethylene purification for lubricating oil manufacture).

<u>Composition</u>:

Cr_2O_3	approx. 95%
Ni	" 5%

<u>Preparation</u>: 50 kg. of chromic acid anhydride (CrO_3) in 20 litres of water are mixed with 9.24 kg. of nickel nitrate ($Ni(NO_3)_2.6H_2O$) in a stainless steel (V2A) mixer. The slurry is evaporated with continuous stirring (by hand, with special spades) until no more nitrogen oxides are given off. The material is then heated in a muffle furnace for 12 hours at 300°C before breaking into 8-10 mm. granules. The granules are reduced by heating for 12 hours at 400°C in a stream of hydrogen (high space velocity no recycle of H_2). The product is cooled under a stream of nitrogen and stored under nitrogen.

<u>Sample</u>: No. 20.

Catalyst 4821

<u>Use</u>: Polymerisation of isobutylene to iso-octylene. (For gases low in isobutylene concentration (20-30%).)

<u>Composition</u>:

Asbestos (serpentine, long fibre Canadian, unwashed; later Russian or Finnish).	Approx. 25%
P_2O_5	Approx. 75%
Water	4-5%

<u>Preparation</u>: 16 litres of phosphoric acid is heated at 260°C for 3 hours and then mixed with 8 kg. of asbestos. The mixture is hand-formed into 1-cm. cubes, which are dried for 60 hours at 150°C. The resulting catalyst is very hard.

<u>Samples</u>: Nos. 34 and 35.

Catalyst 5058

<u>Use</u>: Vapour-phase hydrogenation of middle oil to gasoline.

<u>Composition</u>:

WS_2

<u>Preparation</u>: Tungstic acid ($WO_3.H_2O$) is dissolved in the mother liquor from a previous preparation by gassing with NH_3 at a temperature

below 60°C. The solution is precipitated with H_2S, cooled, and the $(NH_4)_2WS_4$ filtered under vacuum. The crystals are dried in a nitrogen stream on the filter at room temperature, and then converted to WS_2, NH_3 and H_2S by heating at 450°C in a stream of hydrogen in a scroll-type furnace. The resulting WS_2 is ground in a mill and pressed into 10 mm. pellets under a nitrogen atmosphere.

Quantity: Made up to May 1, 1944 - 25 tons per month.

Samples: Nos. 30, 31, 32, and 33.

Catalyst 5436 (Identical with Catalyst 5931 except that caustic is from a different source. No. 5939 uses the same Al_2O_3 as 5436 with only 5% MoO_3).

Use: Conversion of paraffinic gasoline into aromatic and isoparaffinic hydrocarbons - HF or DHD processes.

Composition:

Al_2O_3	90%
MoO_3	10%

Preparation: Catalyst 5780 (see below) in cubical form is soaked once with ammonium molybdate solution, then dried. The solution is so prepared that the above composition of catalyst results.

(Note: For 5436 or 5931, use about 20% MoO_3 in 25% NH_4OH. For 5939, dilute with water.)

Quantity: 10 tons per month.

Sample: No. 44 - Catalyst 5931.

Catalyst 5623

Use: Toluence synthesis from benzene and methanol.

Composition:

P_2O_5	60%
ZnO	6%
Acid-treated clay (Montmorillonite type)	3%
Kieselguhr (Hanover No. 120R fused with NaCl and washed with HCl).	25%
Water	Balance

(any ignited kieselguhr can be used)

Preparation: 44.1 kg. of kieselguhr, 9.0 kg. ZnO, 4.5 kg. clay and about 130 litres of 85% phosphoric acid are mixed in a kneader for about [illegible] minutes, placed on trays, dried for about 10 hours at 300°C, broken up and finally screened.