

**FILM STUDY GROUP**  
**REPORT ON MICROFILM REEL NO. 19**  
**Prepared by**  
**SHELL DEVELOPMENT COMPANY**

# SHELL DEVELOPMENT COMPANY

DATE

Dec. 17, 1945

TO

SHELL DEVELOPMENT COMPANY, SAN FRANCISCO

FROM

~~SHELL DEVELOPMENT COMPANY, EMERYVILLE~~

SUBJECT

U. S. TECHNICAL OIL MISSION, MICROFILM ROLLS 19, 20, AND 21

Attached are reports on Rolls 19, 20, and 21 (Series A) of the Technical Oil Mission microfilm, as requested in Mr. A. E. Miller's letter to you of October 23. These reports have been prepared under the plan set up jointly by the Petroleum Industry War Council and the Petroleum Administration for War.

There is considerable material of potential value to the oil industry in these films. The more significant items have been specifically noted, and have often been abstracted in some detail. Three of the important reports on Fischer-Tropsch synthesis are in English in the films, and these have been accorded very brief abstracts. No detailed translations have been made, but all the items have been abstracted. We have preferred not to assign value ratings to individual items because of the difficulty in deciding what might interest others.

We are returning the microfilm rolls under separate cover.

  
W. J. Hund

HHV

HHV/jrh

Attach: Report on Roll 19  
Report on Roll 20  
Report on Roll 21

cc: (with attach)

- 20 - Shell Development Company, San Francisco, Attn. Mr. Westermann
- 1 - Shell Development Company, San Francisco, Attn. Mr. Kunreuther

Report on Roll 19 (Series A) of  
U. S. Technical Oil Mission Microfilm

This roll reproduces technical documents seized at the Leuna plant of the Ammoniakwerk Merseburg, GmbH (I.G. Farbenindustrie subsidiary).

It contains an unusually large amount of information which may be of interest to the petroleum industry. Though no complete translations have been prepared, some of the documents have been abstracted with sufficient detail to give much of the important information contained in the originals. Several documents are here called to the attention of readers because they are unusually comprehensive and interesting:

1. The Hydroforming Process (1943) p. 1141-1261. This report covers development work up to commercial application. Though German practice on plant scale was probably behind American development in most respects, the development work and research may be of interest. A brief discussion of the German hydroforming process has already been given in T.A.C. Report No. HfMC-2, July 1, 1945.

2. Preparation of m-xylene p. 1460-1463. This patent application describes a process for removing m-xylene from xylene mixtures by selective hydrolysis of its sulfonate.

3. Preparation of Toluene by Catalytic Dealkylation of Higher Boiling Aromatics (1944) p. 1507-1529. Though the application to the production of toluene may not be of immediate interest, the dealkylation of aromatics is of considerable importance. The report gives much information on catalysts, operating conditions and possible mechanisms.

4. Report on the Synol Synthesis (1941) p. 1574-1595. This study of iron catalysts may be quite interesting.

5. Exchange of Information on Fischer-Tropsch (1938) p. 1793-1964. This report, which is in English, covers developments only to 1938, but it presents this information in an unusually complete form. There are several other reports covering the same exchange discussions, also in English, on roll 20 and there is much duplication. This is probably the most complete picture available on the status of Fischer-Tropsch synthesis as of 1938.

Some other potentially valuable subjects included in the roll are:

1. Production of butadiene by thermal cracking of naphthenes.
2. Means of adapting leaded aviation gasolines for use in motor vehicles.
3. Patent applications on various methods of preparing aromatics.
4. Various methods of producing toluene and xylenes.
5. Alcohol production from CO and H<sub>2</sub>.
6. Lacquer from oxidation of wax.
7. Detergents that are salts of monoesters of dicarboxylic acids.
8. Patent applications on reactor designs.

All subjects are covered by the following abstracts, which are quite brief except for the hydroforming work and the catalytic dealkylation of aromatics.

Roll 19 - Abstracts

Bag 3042 (continued)

Target 30/4.02, Ammoniawerk Merseburg, GmbH, Leuna

D) DHD and HF Processes (hydroforming).

p. 1043-1050 Catalyst removal from the HF plant at Moosbierbaum in August, 1943.

The catalyst had been used from July 15, 1942 to August 19, 1943 with 68.5% or 6587 hours operating time. The average cycle time was 11-1/4 hours. It was found that larger pieces of catalyst were not effective in the center. In some cases regeneration time was too short to burn out the carbon from the center of the particle, while in others the hydrocarbons did not appear to have penetrated and reacted beyond a thin outside layer. Catalyst losses varied from 5% to 10% for catalyst 5939. The mechanical stability was excellent. It was recommended to decrease the particle size to 5-6 mm. diameter. Photographs of the split catalyst particles are included in the report which also indicates that catalysts 5633, 5989, 5981, and 6164 were used in this plant.

Moosbierbaum, October 28, 1943

p. 1051

Organization chart of the HF and auxiliary plants at Moosbierbaum.

Moosbierbaum, July 17, 1943

- p. 1052-1054 Analysis of average samples sent from the Moosbierbaum HF plant to Leuna. The recycle gas contained 53%v hydrogen and 21%v methane. The stabilizer tops contained 37%v propane, 12.5%v isobutane, 18.5%v n-butane and small quantities of unsaturates.

Leuna, June 21, 1947

- p. 1055-1062 Plans for turnaround of the Moosbierbaum HF plant including miscellaneous correspondence concerning samples and catalyst delivery.

Moosbierbaum, June 10, 1943  
and earlier.

- p. 1063-1065 Discussion on the DHD (Dehydrierung-Hoch-Druck) and HF (hydroforming) processes. Plants at Leuna, Moosbierbaum, and Pölitze. This is concerned with corrosion problems, mechanical breakdown of the top catalyst layer which is prevented by covering the catalyst bed with a layer of Raschig rings, yields from Hungarian and Romanian gasolines, operating conditions, reactor design, etc.

Moosbierbaum, May 8, 1943

- p. 1066-1067 Analyses of hydroformed gasoline from Moosbierbaum. Octane number was 80.5 to 81, and aromatic content was 51-53%.

January 28, 1943

- p. 1068-1123 Monthly summary of operating data for the Moosbierbaum hydroforming plant. Contains inventory data on charge and products, production figures, intermediate yields, schematic flowsheets with material balance.

November, August, July, and June, 1944.

- p. 1124-1126 Patent application: Hydroforming. Use of catalysts of different particle size where the incoming charge passes through progressively smaller catalyst particles with possible intermediate heating. The purpose is to maintain constant temperature by contacting the highly reactive charge with catalyst of low surface area per unit volume. Size decreases from 16 to 4 mm. A considerable increase in aromatization is claimed over work with uniform particle size.

Ludwigshafen, June 17, 1944

p. 1127-1129 Patent application: Dehydrogenation (butane). Drying the catalyst after regeneration, with dry air or other gases to reduce the moisture content to 0.1-0.3% permits lower temperature operation, less disproportionation and increased catalyst life. Ludwigshafen, June 16, 1944

p. 1130-1136 Patent application: Cracking and hydroforming (endothermic reactions) where the reaction temperature is maintained constant by the use of intermediate heaters or the recycling of gases containing less than five carbon atoms. Ludwigshafen, December 21, 1940

p. 1137-1140 Patent application: Hydroforming catalyst where aluminum is dissolved with aqueous caustic and activated with a 1% mercury salt solution. This solution is treated with diluted acetic acid, removed from residual aluminum, evaporated and dried to a glassy mass at 600-700°C. 900 g. of this alumina in granular form are soaked in aqueous solution containing 136 g. of ammonium-molybdate and then dried. This alumina is supposed to give better yield and quality. Ludwigshafen, July 9, 1940

p. 1141-1261 The hydroforming process: This is a detailed descriptive report of the development and results obtained up to the application on commercial scale at Moosbierbaum.

Leuna, February 12, 1943

A. Basic conditions: Charge: all kinds of gasolines boiling up to 165°C; process period: more than 10 hours; temperature: about 500°C; pressure: 15-30 atm. in the presence of H<sub>2</sub>; catalyst: MoO<sub>3</sub> on alumina; chemical reactions: formation of aromatics, cracking and isomerization.

B. Experiments in an electrically heated, single tube reactor: Catalyst studies: The most active alumina carrier was found to be one prepared by dechlorination of aluminum chloride by heat. Of the precipitated aluminas only those prepared at a pH of 6.5 or less were active which was only possible for the catalysts 5358 and 3252 but not 2345 which is precipitated with CO<sub>2</sub> from aluminate. All aluminas can be activated by heat or peptization with acids or ammonia. It was found that two methods produced particularly active aluminas: precipitation with ammonia from the nitrate and subsequent peptization with nitric acid, or precipitation with nitric acid from aluminate. Formic acid was as good as nitric acid for peptization. The aluminate type was finally chosen. 10% MoO<sub>3</sub> was found to be the optimum concentration and it

was found that as little as 0.1% alkali and alkali earth impurities had a noticeably detrimental effect on catalyst activity. On the other hand  $Fe_2O_3$  and  $SiO_2$  did not affect the catalyst in concentrations of about 1%. It was found that smaller particle sizes gave longer reaction periods at lower temperature but this was only true if the  $MoO_3$  was added after the particles had been broken up.

Operating conditions: The effect of temperature is discussed in considerable detail. It is emphasized that it has to be maintained within 2-3°C to prevent excessive fluctuation of the aromatics content. Influences of temperature gradients through various reactors (adiabatic, heated tubes, etc.) on the rate of aromatics formation are discussed. It was found that the cycle length could be increased at constant average temperature if a uniform gradient was maintained with a temperature at the reactor exit 10°C above the average.

Increasing pressure increases the cycle length by reducing the coke formation even though the temperature has to be increased. However, the more paraffinic the charge is, the more cracking results with increasing pressure, thus decreasing the yield. Therefore the optimum pressure depends on the type of charge used.

Space velocity was optimum at 0.7-0.8 v/v/h for paraffinic charges at 15 atmospheres and at 0.8-1.0 v/v/h for naphthenic charges at 30 atmospheres.

A high recycle gas to charge ratio is very desirable because it not only increases the hydrogen partial pressure but also facilitates the vaporization of the high boiling products formed thus decreasing adsorption on the catalyst and coke formation.

C) Pilot Plant Experiments.

Two reactor types were investigated: an adiabatic reactor (3 vessels in series, each 6 inch diameter and 9 ft. long, insulated, and surrounded with hot air, with interstage heaters) and a gas heated tubular reactor (five 19 foot lengths of 3-1/2 inch pipe heated by hot flue gases from a furnace). Experimental work is described in detail.

Though the simpler adiabatic reactor was used in the commercial plant at Moosbierbaum it was found that the heated tubular reactors were superior, increasing the yield 4-5%, reducing coke formation and increasing the plant capacity by 75%. The possibility of putting adiabatic reactors in series with and behind heated tubular ones was considered promising.

D) Experiments with Pure Hydrocarbons.

Experiments with paraffins and naphthenes confirmed the conclusions reached from work with different gasolines. Aromatics seem to be primarily dealkylated with a small amount of condensation and cracking also taking place, particularly at higher pressures in the order of 50 atmospheres. It was concluded that naphthene formation was not an intermediate in the hydroforming of paraffins. Considerable isomerization was observed which, particularly in the case of the higher boiling paraffins (heptanes +) occurred without excessive cracking. On the other hand, paraffins with two side chains were largely back-isomerized to single branch paraffins.

E) Product Quality and Composition.

The percentage of aromatics formed from paraffins was deduced from the experiments with pure hydrocarbons and operating results. The xylene fraction contained a relatively small percentage of the undesirable ortho isomer. Few aromatics other than toluene and the xylenes were found.

The dependence of the 3-C rich and lean mixture ratings on aromatic content was established and changes in the steepness of the curves discussed.

Though the storage stability of the unleaded gasoline was satisfactory (bomb test) only sulfuric acid treated material gave passing tests for leaded gasoline. It was interesting that Fuller's earth treatment yielded gasoline which though it gave a poor bomb test, had excellent stability on actual storage in glass.

Bottoms could be used in two ways: fractionated to produce a 200°C E.P. motor gasoline, degrading the 200° + material to diesel fuel; or using the material boiling up to 220°C as a lacquer solvent. Another use would be the rehydroforming of the bottoms at 50 atm., or over a special catalyst at 100-200 atm. (probably 1% MoO<sub>3</sub> on alumina) yielding gasolines containing from 70 to 90% aromatics thus increasing the yield of aviation fuel 2-4% and the overall aromatics content 2-3%.

F) Patent and Literature Survey.

Several I.G. applications are listed but those considered "secret" are not included.

G) Appendices.

The large number of curves, tables, and sketches include catalyst evaluations and codes. The catalysts are various synthetic and natural aluminas, containing MoO<sub>3</sub> and in some cases additional components.



p. 1262-1270 Discussion on the Status of the DHD and HF Processes.

This report includes a considerable amount of pilot plant data on both natural and synthetic gasoline with special emphasis on the effect of temperature variations in adiabatic reactors. It was found that the inlet temperature should be progressively increased for three series reactors. High temperature should be avoided and the temperature drop in a reactor should not exceed 25°C. The effect of higher pressures was investigated. The recycle gas rate should be at least 1 m<sup>3</sup>/kg oil and better 1.5. The space velocity should not exceed 0.5 kg/liter/hr.

Another group of investigators studied adiabatic and isothermal reactors. For different types of gasolines, operating conditions and yields were determined. In three series reactors the aromatics formation was distributed 45%, 30%, 25% by proper temperature control. In isothermal reactors the optimum conditions were determined. Regeneration time was 25%, maximum, of the reaction time with 2.5 m<sup>3</sup>/liter/hr. recycle gas space velocity.

The report of data is followed by discussion of the results. Leuna, June 18, 1942

p. 1271-1290 Investigation and Comparison of Bottoms from the DHD and HF Processes.

This report contains detailed analyses of the two bottoms products with an attempted analysis for individual hydrocarbons. It was found that the HF bottoms (lower pressure) contain a higher percentage of aromatics boiling below 210°C which consist primarily of substituted benzenes. Except for the degree of substitution of the naphthalene no major differences were found when comparing equal boiling range fractions. Some discussion on the formation of these bottoms and their behavior on conversion to gasoline is included. Leuna, July, 1944

p. 1291-1316 Catalytic Dehydrogenation and Cracking in the Presence of Hydrogen.

This report includes a summary of experiments on the above subject carried out mostly in the vapor phase over solid catalyst but also with finely divided catalyst suspended in a high boiling oil. Experiments were performed at pressures from atmospheric to 200 atm. Several catalysts were investigated. Ludwigshafen, June 24, 1939

E. Refining Processes Misc.

p. 1318 Notes from a discussion in Leuna on August 5, 1943, on the treatment of gasoline from the carbonization of coal over tungsten-nickel-sulfide (Catalyst 5802) at 50 atmospheres. Temperature, at first 465°C, is increased to 510°C at end of run. Gasification is about 2-3% and the formation of esters 5% because of the high oxygen content. Recycle gas 5000 v./v. oil. Space velocity 0.5-0.6 v./v./h. Process starts exothermic and becomes endothermic at the end. Auschwitz, August 11, 1943

p. 1320-1321 Additional information on the same subject as page 1318. Leuna, August 8, 1943

p. 1322-1323 Problems in connection with the carbonization of bituminous coal. This is a statement of some unsolved problems such as conversion of gas oils from coal to high octane gasoline and recovery of resins from coal tar. Leuna, May 13, 1943

p. 1325-1326 Dewaxing plant at Moosbierbaum. Discussion of a new process which is not described in detail. Oil is removed from the mixture of soft and hard wax and the two are subsequently separated. The hard wax thus obtained can be used directly for cracking and oxidation while the soft wax is used for floor wax. The soft wax produced by the Edeleanu process is of inferior quality.

The solvent used is a mixture of tetrahydrofuran, methanol and toluene while Edeleanu has so far only used a mixture of methylene chloride and dichloroethane.

The report then continues with the consideration of a possible agreement with Edeleanu. Leuna, February 22, 1944.

p. 1327-1336 Kuckuck project. Discussions of an underground refinery identified by the above code name located at a place identified as "NSW" (apparently Niedersechswerfen). Includes information on the types of plants to be built without going into very intimate technical details. Other correspondence concerning this project includes plants for experimental work with the catalytic cracking unit (moving bed type) planned for the project, space and equipment requirements, etc. Leuna, 1944

p. 1387-1361 Preparation of Butadiene by Thermal Cracking of Naphthenes or Hydrogenation Products Rich in Naphthenes.

This is a detailed descriptive report containing the following conclusions: By internal electric heating in the liquid phase high yields of butadiene can be obtained without the use of diluents. For heating, molybdenum, tungsten, tantalum, or platinum wire coils are suitable. Up to 30% butadiene is obtained from naphthenes obtained by the hydrogenation of phenols.

Several solvents were tried for the concentration of naphthenes by extraction. Of the solvents tried Chlorex (beta, beta'-dichlorodiethyl ether) appeared most promising. SO<sub>2</sub> was going to be tried at higher temperature and pressure.

Leuna, September 28, 1938

p. 1362-1364 Apollo Refinery at Bratislava. A very short descriptive report. Distillation, Dubbs cracking, lubricating oil.

Leuna, April 8, 1943

p. 1365-1404 Removal of TEL from aviation gasoline to make it usable for motor vehicles.

An attempt was apparently made to convert some leaded aviation gasoline to motor fuel. Various methods for removing TEL were proposed, including hydrogen chloride gas (danger of insoluble lead compounds if removal is incomplete), and activated charcoal. The addition of ethylene dibromide (about 0.5 cc./liter) to the leaded gasoline was partially successful in overcoming harmful effects. There is a considerable amount of correspondence discussing many proposed methods and results. Letters and memoranda from various sources, 1943.

F. Preparation of Aromatics.

p. 1406 Distillation curves in the presence and absence of methanol of an extract from the 100-115°C fraction of a hydroformed gasoline (88.5% aromatics)

p. 1407-1413 Patent application: Preparation of toluene and other alkyl benzenes by alkylation of benzene with methanol and/or ethanol over a phosphoric acid-zinc oxide catalyst where the phosphoric acid is present in excess of the amount needed for the formation of secondary zinc phosphate and the ester content is not less than 4%.

Ludwigshafen, November 25, 1940

- p. 1414-1419 Patent application: Process for the alkylation of aromatics with methanol, dimethyl ether, olefins or olefin yielding compounds at elevated temperature and pressure over a catalyst prepared by mixing 5-40% kieselgur, 5-30% zinc oxide and 55-90% phosphoric acid and drying at 130-500°C until solidification. See also pages 1449-1453.  
Ludwigshafen, November 25, 1940
- p. 1420-1442 Alkylbenzenes, preparation, properties and use. This report describes experiments on the alkylation of benzene with propylene in the presence of  $H_2SO_4$  which was not stronger than 92%. Yields of 55% cumene (25% diisopropyl benzene) were obtained. Temperatures must be below 10°C. Experiments for the preparation of other similar alkylates is included.  
Leuna, March 24, 1939
- p. 1443-1448 Patent application: Preparation of alkyl benzenes from benzene and higher boiling alcohols from the methanol synthesis in the vapor phase at elevated temperature (320°C) and pressure (500 atm.) over pyrophosphoric acid on asbestos. The hydrogenated product has a very high octane number (115 for the 90-200°C fraction).  
Ludwigshafen, May 16, 1940
- p. 1449-1453 Addition to patent application, pages 1414-1419: Addition of hydrosilicates to the catalyst.  
Ludwigshafen, September 15, 1941
- p. 1454-1459 Patent application: Purification of aromatics by azeotropic distillation where the top product is subcooled in order to separate the solvent as a second layer. Acetonitrile and methanol are among the third components used.  
Ludwigshafen, November 24, 1943
- p. 1460-1463 Patent application: Preparation of pure m-xylene. A xylene mixture is sulfonated with 80%  $H_2SO_4$ . The unreacted hydrocarbons are removed and the remaining middle and lower layer diluted with water, heated to 130° and then steam distilled with steam superheated to about 140°C maintaining a temperature of 140-142°C. Under these conditions only the m-xylene sulfonic acid is hydrolyzed.  
Ludwigshafen, November 30, 1943
- G. Proposed Manufacture of Toluene.
- p. 1465-1466 Secret Patent: Briehmer and Heurin, Partial dealkylation of polymethylbenzene by treatment at 600 to 900°C with hydrogen over a catalyst consisting of phosphoric acid or phosphoric pentoxide on a carrier such as coke.

- p. 1467-1470 Toluene Purification: Discussion of distillation requirements for the production of nitration grade toluene.  
Leuna, October 12, 1942
- p. 1472-1476 Preparation of a toluene fraction (Leutol) from the 100-115°C cut of hydroformed gasoline by extraction with SO<sub>2</sub> and azeotropic distillation with methanol. Includes flow diagram with material balance.  
Leuna, November 23, 1942
- p. 1477-1481 Discussion in Waldenburg of the possibility of further processing the Leutol in a Witol plant for the preparation of pure toluene.  
Leuna, December 17, 1942
- p. 1482-1484 Discussion and description of a dealkylation process for the production of toluene from higher boiling aromatics. The 115-250° fraction of hydroformed gasoline is dealkylated at 200 atmospheres and 460-480°C in the presence of an aluminum silicate type catalyst and hydrogen. Space velocity is 0.5-1.0 Kg/liter catalyst/h. The recycle gas volume is about 5000 times the liquid charge volume. The product contains about 50% toluene plus benzene (2/3 toluene) and 50% higher boiling aromatics which are recycled. Methane is purged by scrubbing of the recycle gas.  
Leuna, January 14, 1943
- p. 1485-1486 Flowsheets for the dealkylation of xylenes and higher.  
January 14, 1943
- p. 1487-1488 Cost analysis for a xylenes and higher dealkylation plant. The catalyst mentioned in this report is similar to hydroforming catalyst consisting of less than 5% molybdic acid on precipitated alumina. Leuna, January 25, 1943
- p. 1489-1490 Discussion of toluene and xylene supply for explosives.  
Berlin, January 29, 1943
- p. 1491-1494 Description and Evaluation of the Ruhrchemie process for the production of toluene from heptane: This is an attempt by the I.G. to figure out what Ruhrchemie was doing, chiefly on the basis of published literature on heptane dehydrocyclization. They believe that heptane is aromatized at low pressure and low space velocity over CrO<sub>3</sub> on alumina catalyst at temperatures between 450 and 520°C. Yields of 65-75%w of the heptane charge appear possible.  
Leuna, April 7, 1943
- p. 1495-1496 Use of xylenes for explosives: Non-technical discussion on the availability and quality of xylenes, methods of producing them and of converting them to toluene.  
Berlin, April 22, 1943

p. 1497-1499 Purification of toluene from coking operations by dehydrogenation over catalysts 58/II and 5931 (hydroforming) followed by fractionation. 5931 appeared to be more desirable.  
Leuna, June 18, 1943

p. 1500-1501 Recovery of toluene from the hydroforming plant at Moosbierbaum and other I.G. plants (not much technical information)  
June 22, 1943

p. 1502 Discussion of proposed toluene production by dealkylation of xylenes and higher aromatics (1400 tons/month).  
Pressures between 100 and 200 atmospheres are mentioned and space velocities of 0.8 to 1.0 Kg/v./h. The hydrogen consumption is estimated at 400 m.<sup>3</sup>/ton of dealkylated products.  
Leuna, November 16, 1943

p. 1503-1529 Detailed report on production of Toluene by catalytic dealkylation of higher boiling aromatic hydrocarbons.  
Leuna, October, 1944.

The process is an outgrowth of the "Arobin" process for the production of aviation gasoline from hydroformer bottoms. Two types of catalyst were considered: MoO<sub>3</sub> on alumina and on aluminum silicate. The former appears to operate by splitting the alkylbenzene into methane and the aromatic with one less methyl group while the latter causes disproportionation, producing a molecule of toluene and one of trimethylbenzene from xylene. This process continues and at the same time isomerization apparently causes the conversion of short side chains to longer ones. Since aromatics with long side chains are less stable they hydrocrack to lower boiling aromatics and propane or butane which are found in considerably larger quantities with the silicate catalyst than is methane.

The process was to be applied to bottoms from the toluene plant at Waldenburg where toluene is produced from benzene and methanol ("witol").

Alumina catalysts:

a) Hydroforming catalyst (10% MoO<sub>3</sub> on alumina) caused too much hydrogenation at 50 atmospheres and 440-460°C but the action improved at temperatures between 485 and 505°C. The maximum permissible pressure was 75 atmospheres above which hydrogenation of aromatics became excessive. At 50 atmospheres and a space velocity of 0.6 v./v./h. 45-50% conversion was obtained and regeneration became necessary after about 14 days. At 75 atmospheres continuous operation was possible with a space velocity of 1.0 v./v./h. The toluene yields were 0.15 and 0.21 Kg toluene/liter catalyst/hr.

b) Reducing the MoO<sub>3</sub> on the alumina to 1%, the same toluene yield could be achieved at 100 atm. as at 75 atm. with hydroforming catalyst, permitting continuous operation in spite of the reduced hydrogenation activity of the catalyst.

c) With all alumina catalysts the toluene yield was the same, about 54-55% of 100-115°C fraction. The lighter tops were 18-20% containing 60-70% aromatics. The gas formed at temperatures of 485-495°C consisted principally of methane and ethane.

d) Cr<sub>2</sub>O<sub>3</sub> gave no improvement and was not as stable.

e) The experiments mentioned above were carried out with pure hydrogen. Larger scale experiments with recycle gas containing 40% hydrocarbons required the following conditions for continuous operation:

	Pressure (atmospheres)	Temperature (°C)	Space Velocity (Kg/v./hr.)
Hydroforming Catalyst	100	505	0.9
1% MoO <sub>3</sub> on Alumina	200	505	0.9

Attempts to operate with recycle gas at 50 atmospheres indicated that with 20-25% hydrocarbon in the gas, the operating time was 120-140 hours while it was only 40-60 hours when the hydrocarbon concentration was increased to 30-35%. The difficulty with this type of operation will be to remove methane efficiently in order to maintain a sufficiently low hydrocarbon concentration.

f) Products: About 14-16% methane (based on conversion) was formed and 2-6% higher boiling hydrocarbons. The lower percentages are applicable to 50 atmospheres operation while the higher ones are obtained at 200 atmospheres. Distillation of the 100-115°C fraction in a packed column (13 theoretical plates) yielded a nitration grade toluene (2°). 60%w of this fraction was obtained (76% of theoretical) of which 7% was already in the charge.

g) Heat: The reaction is exothermic requiring the removal of 150-200 Kcal. per Kg. of toluene formed.

#### Aluminum silicate catalysts:

a) Synthetic aluminum silicate containing 1% MoO<sub>3</sub> gave best results. Higher molybdenum concentrations resulted in excessive hydrogenation at 200 atmospheres,



and pressure therefore had to be reduced for such catalysts, which caused coke formation and resulted in maximum reaction times of 14 days for 5% MoO<sub>3</sub> at 100 atmospheres. MoO<sub>3</sub> contents below 0.5% at 200 atmospheres also caused coke formation and a reaction time of 14 days. Since these catalysts are sensitive to frequent regeneration, discontinuous operation should be avoided.

b) Yields: Toluene yields are lower than with alumina catalyst; about 40%w was produced of which only 35% was recovered by distillation. Substitution of Cr<sub>2</sub>O<sub>3</sub> for MoO<sub>3</sub> increased the yield 5-8% but coke formation occurred on the catalyst which could not be regenerated without excessive loss of activity. Recycle operation confirmed the poor yields and also showed that the hydrocarbon gases were practically exclusively propane and butanes.

c) Addition of benzene: Because of the disproportionation reaction it was thought that benzene would increase the yield of toluene. At 460°, 0.6 v./v./hr., benzene: xylene = 1:2, an increase in toluene yield of 7-8% was observed. However only 20-30% of the benzene was converted, mostly to toluene. Since at these high temperatures the dealkylation of xylene is dominant, experiments were made at 300-420°C. Unfortunately reaction rates were too low at these temperatures.

#### Fuller's Earth Catalyst.

A catalyst containing 5% MoO<sub>3</sub> on fuller's earth from Moosbierbaum yielded a high percentage of toluene with continuous operation. However the hydrogenation was considerable so that azeotropic distillation would be required to produce nitration grade toluene. With a different fuller's earth (Frankonit H) considerable hydrogenation was observed even with only 1% MoO<sub>3</sub>. This catalyst was not considered desirable.

Use of xylene-free bottoms (IBP 165°C), which were practically 100% aromatic, for toluene production was not very successful at 50 atm. and 485°C giving low toluene yields. This indicates that losses increase rapidly as the number of CH<sub>3</sub> groups to be split off increases. Similar results were obtained with hydroformer bottoms where 30-35% of 100-115°C fraction was recovered containing 92% toluene. Coke deposition occurred in both cases and the reaction period was 20 hours at 50 atm. and 50 hours at 100 atm.



Use of a "solvent benzene" derived from the coking process, having a boiling range of 167-191°C, and containing 12% olefins as well as 7% paraffins or naphthenes and traces of phenols and pyridine was attempted. With hydroforming catalyst at 100 atm. and 495-505°C, 40-50 hour reaction periods were obtained when operating with circulating hydrogen containing 40% hydrocarbons. Yields were much poorer than with toluene plant bottoms, possibly because of the large amount of non-aromatic material. A 82% yield of 100-115°C fraction was obtained containing 90% toluene.

An aromatic fraction from tar yielded large amounts of toluene when processed under ordinary hydroforming conditions, while treatment over tungsten-nickel sulfide caused only sulfur removal, olefin saturation, and, at higher temperatures, cracking.

Data sheets are appended in the report.

#### H. Alcohol synthesis from CO and H<sub>2</sub>.

p. 1580-1561 The use of Zinc and Chromium as Catalysts for the Methanol Synthesis: Leuna, January 25, 1928

Of the zinc minerals, flowers of zinc soaked in chromic acid yielded a catalyst equal to the ordinary one. This was followed by "Adamin" which, after reduction with hydrogen for the removal of arsenic, and impregnation with chromic acid, was equal to the first one. Both catalysts are more stable than the normal catalyst. The other zinc compounds investigated were inferior. Chromium minerals impregnated with zinc salts are unsatisfactory because the chromium is not in the right stage of oxidation and the zinc oxide content is too low. It was shown that catalysts on zinc oxide bases are most satisfactory, but that it would be desirable to protect the use of minerals by addition to existing patent application. The catalyst used commercially is composed of zinc oxide, magnesia and chromium.

p. 1562-1573 Experiments to increase the mechanical strength of methanol catalysts. - Second report. Leuna, January 5, 1928

A very much improved catalyst was developed by preparing a paste from zinc oxide and magnesium chloride solution which was dried, calcined, and the porous pieces obtained soaked in chromic acid solution. The manufacturing technique for the new catalyst (No. 288) is described. It was later found that the substitution of magnesium nitrate for the chloride gave even better results (No. 355).

The observation that a very small magnesia content (less than 2%) increases the strength of zinc oxide catalyst appreciably led to the thought that it may be applied to other catalysts. Thus a very good catalyst was prepared for the isobutyl synthesis by impregnating a zinc oxide-magnesia carrier with potassium dichromate. It was better than the fused zinc oxide dichromate catalyst. The use of rotating drums with magnesium chloride solution injection appears very promising for the preparation of strong spherical catalyst.

p. 1574-1595

Report on the Synol Synthesis. Leuna, May 2, 1941

Cobalt Catalyst: At 190°C, 10 atm. pressure and a space velocity of 100, the 200-300° fraction contained 27.2%w alcohols and the 300-350° fraction 22.2%.

Iron Catalyst development: It was found that re-fusing of fused iron catalyst in an electric arc increased its alcohol forming activity. Precipitated iron catalysts were mechanically weaker than the fused catalysts. The most active two component precipitated catalyst consisted of 96.5% Fe<sub>2</sub>O<sub>3</sub> and 3.5% Al<sub>2</sub>O<sub>3</sub> (No. 2643) and yielded 20% 230-350° fraction containing 42.5%w alcohols. The next best one was composed of 99% Fe<sub>2</sub>O<sub>3</sub> and 1% Mn<sub>2</sub>O<sub>3</sub> (No. 2844) and yielded 15.4% 230-350° fraction containing 30%w alcohols. Another good catalyst was 99% Fe<sub>2</sub>O<sub>3</sub> and 1% ZnO (No. 2700). It was noted that concentrations above 3% of the second component gave progressively lower activity. Alcohol production increases with decreasing reaction temperature. In most cases the alcohol production decreases rapidly with time, being about half of the initial after 10 days. This seems to be caused primarily by the increased temperature. Exceptions to this rule are for example catalyst 2643 where the alcohol production decreases only slowly and a catalyst consisting of 99% Fe<sub>2</sub>O<sub>3</sub> and 1% Ni<sub>2</sub>O<sub>3</sub> (No. 2918) with which alcohol production slowly increases during the first 30 days. Several catalysts were found which produce considerable amounts of alcohols in the gasoline range and lighter; these include: 95% Fe<sub>2</sub>O<sub>3</sub> and 5% Ni<sub>2</sub>O<sub>3</sub> (No. 2919) and 95% Fe<sub>2</sub>O<sub>3</sub> and 5% ZnO (No. 2660). The most active catalysts are hard to control at first and it is therefore difficult to prevent coking. Attempts will be made to dilute these catalysts by means of carriers.

Wax oxidation: It was found that a usable lacquer coating could be prepared from Fischer wax by oxidation with air at 150-170°C. Only high melting waxes are applicable, particularly those melting above 103°C. Oxidation time is between 20 and 30 hours.

- p. 1596-1607 Patent Application: Formation of alcohols from CO and H<sub>2</sub> where hydrocarbons are added to the mix to increase the alcohol yield.  
Ludwigshafen, August 19, 1941
- p. 1608-1618 Patent Application: Formation of oxygenated products from CO and H<sub>2</sub> where the reaction is carried out in more than one stage in order to increase the yield of oxygenated products, and in such fashion that the CO<sub>2</sub> content of the gas after each stage does not exceed 15% of the liquid and solid-free tail gas.  
Ludwigshafen, September 23, 1941
- p. 1619-1630 Patent Application: Reduction of reaction temperature in Fischer-Tropsch Synthesis by carrying out the reduction of the iron catalyst at high hydrogen velocities in the order of 3000 m<sup>3</sup>/hr/m<sup>3</sup> catalyst and by limiting the CO<sub>2</sub> formation in each stage (based on liquid and solid-free tail gas) to not more than 20%.  
Ludwigshafen, September 24, 1941
- p. 1631-1639 Patent Application: Increasing yield of alcohols by Fischer-Tropsch by maintaining the temperature so low that at most 70%, preferably less than 50%, of the heat of conversion is liberated, thus reducing methane formation.  
Ludwigshafen, February 27, 1942
- p. 1640-1646 Patent Application: Production of hydrocarbons and alcohols by Fischer-Tropsch over iron catalysts, where the pressure is maintained between 12 and 25 atm. in the vapor phase (without liquid addition) and with rapid removal of the heat of reaction. Ludwigshafen, March 27, 1942
- p. 1647-1655 Patent Application: Production of hydrocarbons and alcohols by Fischer-Tropsch over iron catalyst, where the pressure is maintained between 35 and 55 atm. in the vapor phase (with washing of the catalyst with added liquid) and with rapid removal of the heat of reaction.  
Ludwigshafen, March 27, 1942
- p. 1656-1660 Addition to Patent Application: Separation of mixtures of alcohols and hydrocarbons by adsorption on a solid and stripping either with steam or hot gases such as hydrogen.  
October 6, 1942
- p. 1661-1664 Draft of the above application.  
Leuna, October 5, 1942
- p. 1665-1674 Patent Application: Recovery of organic products in the aqueous layer from steam stripping of adsorbents.  
Ludwigshafen, February 3, 1943

p. 1675-1679 Patent Application: Prevention of emulsions during scrubbing of the oil layer (obtained from steam stripping of adsorbed Fischer-Tropsch products) by using the aqueous layer for scrubbing in place of fresh water.  
Ludwigshafen, March 16, 1943

p. 1680-1683 Patent Application: Oxo process using as a charge a cut of a product from water gas synthesis over iron catalyst at a temperature below 250°C and elevated pressure (medium pressures), said cut containing oxygen compounds and olefins. This charge is treated with CO and H<sub>2</sub> over cobalt-thorium catalyst at about 250 atm. and 135°C. The product is hydrogenated at the same pressure and 180°C. The product is esterified with boric acid and separated from the neutral oils. Straight chain alcohols are primarily formed.  
Ludwigshafen, March 31, 1943

p. 1684-1698 On the salts of dicarboxylic acid monoesters of longer chain alcohols of the Synol and Oxo Synthesis,  
Leuna, January, 1944

Because of their melting and washing properties, the alkali salts of the dicarboxylic acid monoesters are being considered by the textile and laundry industry. One such product is already marketed successfully: the sodium salt of a monoester mixture prepared from succinic anhydride and higher alcohols. It has remarkable washing and capillary-chemical properties. As raw materials oxalic acid as well as dicarboxylic acids of higher carbon content are interesting which permit the use of C<sub>6</sub>-C<sub>12</sub> alcohols from the Synol synthesis.

General Information on the Preparation of Monoesters:

- 1) Direct esterification of the acid with alcohols (published).
- 2) Conversion of diesters to monoesters with free dicarboxylic acid. The products are heated in the absence of moisture (published). This method has been used recently for the preparation of mono-methyladipate.
- 3) Partial saponification of the diester (published).
- 4) Where the anhydride can be prepared, its reaction with alcohol or an alcoholate is practically quantitative.

Oxalic acid: Only partial saponification was successful and even there the yields were very low. The process did not function at all when the salts were water soluble.

Adipic acid: (one page missing) Direct esterification in the presence of Wofatit P is possible, yielding 62% monoester and 38% diester on the basis of the alcohol used. Conversion of diester to monoester with free acid is also possible (Synol C<sub>12</sub> ester) at 250°C. Esters are freed from free acid with pentane and the acid filtered out. The filtrate is washed with a water-methanol mixture. The monoester is then extracted with sodium carbonate solution in the presence of isopropyl alcohol. The ester is re-extracted from the aqueous alcohol solution with pentane and recovered by evaporation of the pentane.

Sebacic acid: same as for adipic acid but lower yields. Tests on washing and wetting properties are included.

#### I. Reactors for Catalytic Processes.

p. 1700-1705 Patent Application: Design of a catalytic reactor where the granular or powdered catalyst passes downward through a series of vibrating screens which can be so controlled as to keep the catalyst height constant,  
Ludwigshafen, April 8, 1943

p. 1706-1710 Patent Application: Design of a catalytic reactor where the reacting gases pass upward through screens and where the catalyst is moved downward from screen to screen by rotating or tilting the screens.  
Ludwigshafen, March 6, 1943

p. 1711-1721 Patent Application: Design of heat exchangers for endo- or exo-thermal reactions where the tubes containing the cooling or heating medium are of the bayonet type, including an inner feeding tube if desired and possibly arranging the tube bundle such that the open ends are higher than the closed ones in order to facilitate the counter-current flow of liquid and vapor.  
Ludwigshafen, October 13, 1942

p. 1722-1730 Patent Application: Design of heat exchanger reactor for exothermic and endothermic processes using solid catalyst arranged around heating or cooling tubes, where the shell is only supported at one end to permit easy removal of the shell and free access to the catalyst without the need to disconnect any piping. Either bayonet tubes or floating heads may be used.  
Ludwigshafen, October 13, 1942

J. Fischer-Tropsch

- p. 1732-1735 Progress report from the Kaiser-Wilhelm-Institute for coal research (Mülheim) by Franz Fischer for the period from April 1, 1941, to March 31, 1942. Contains list of personnel but no technical information.
- p. 1736-1792 Appendix to a report on progress in hydrocarbon synthesis at Leuna during the first half of 1939. This consists of tables of data and graphs on such subjects as: effect of operating variables such as temperature, catalyst, catalyst age, space velocity, CO:H<sub>2</sub> ratio, inerts and additives; Synthesis under pressure; yield summaries, cost analysis, etc. Leuna, September, 1939
- p. 1793-1964 Report on exchange of information on Fischer-Tropsch between I.G., Standard of N. J., Kellogg, and Shell, between October 25 and December 1, 1938. These are notes by the Shell representative, written in English, which cover a visit to, and information received from, Ruhrchemie at their plant at Holten and a discussion between the four companies mentioned above at Ludwigshafen. The report is in great detail with data, sketches, and detailed description of the processes involved as well as information on I.G.'s work with iron catalyst up to that time. The appendices to this report are on Roll 20. No date.