

FILM STUDY GROUP

REPORT

T.O.M. REEL NO. 41

Prepared by

SHELL DEVELOPMENT COMPANY

## SHELL-DEVELOPMENT COMPANY

Report on Reel 41 (formerly 9B) of  
U.S. Technical Oil Mission Microfilm

This reel reproduces technical documents taken from the Ruhrchemie A.G., Sterkrade-Holten, Germany. This company was a leader in the field of Fischer-Tropsch Synthesis, but this film contains little interesting material in this field except for the analytical methods used for plant control and a detailed description of the Ruhrchemie process for synthesizing high V.I. lube from Fischer-Tropsch high boiling primary products by cracking and subsequent polymerization. Among the subjects of interest are:

Analytical procedures for Fischer-Tropsch plant.  
Patent applications on aromatization, catalytic cracking, etc.  
Preparation of synthesis gas and acetylene by cracking methane with steam, carbon dioxide and oxygen.  
Thermal cracking of  $330^{\circ}\text{C}$  + Fischer-Tropsch fraction and polymerizations of the  $\text{C}_6^+$  cracked products to lube oil.  
Propionic aldehyde from ethylene and water gas by the Oxo process.

All material is covered in the following abstracts. These are identified only by the item numbers used in the index and written on the first page of the section. There are no page numbers on this film. It was felt that none of the material warranted detailed abstracting or translating. Value ratings have not been assigned.

Reel 41, Abstracts  
Ruhrcemie A.G., Sterkrade-Holten

Bag 2244 continued  
Target 30/5.01

Item (unmarked) Analysis of C<sub>1</sub> to C<sub>5</sub> Hydrocarbons by Fractionation

The method and equipment are very much like Podbielniak with automatic top temperature control, immersion heater, etc. The second thermocouple junctions are kept in boiling water instead of ice, which gives automatic correction for barometric pressure since the boiling point increase for water and hydrocarbons is nearly the same. Packing consists of an aluminum spiral made by winding 1.7 mm. diameter aluminum wire on a 0.5-0.6 mm. diameter steel wire (226 turns per meter length of steel wire). The outside of the spiral is ground down until it fits exactly into the 3.8 mm. I.D. distillation tube.

Hauptlaboratorium

March 14, 1940

25 pg.

Item 4 Cont. Oil for Hydromatic Drives. Viscosity, viscosity index and other properties are discussed.

Holten

Jan. 5, 1942

2 pg.

Addition and Substitution of Chlorine and Olefins. Pumice, TiO<sub>2</sub> on pumice, iron-containing bauxite on pumice and granulated bauxite were tried with C<sub>2</sub> to C<sub>4</sub> olefins.

I. Gavst, Bukarest

Nov. 3, 1943

1 pg.

Pat. Appl. Synthetic lube oil by polymerization of unsaturated or chlorinated C<sub>7</sub><sup>+</sup> hydrocarbons with hydrofluoric acid.

Rheinpreussen

Jan. 12, 1943

Polymerization Technique, Vol. II excerpts Feb. 13, 1943 4 pg.  
Report on the Lubricant Convention, Dec. 1941 and 1942, excerpts 5 pg.  
Molecular Distillation of Lubricating Oil. Description of continuous improved still operating at 10<sup>-4</sup> mm. Hg. Experiments are described.

Holten

Nov. 23, 1942

22 pg.

Experiments on Heat Transfer in Lubricating Oil Synthesis

Holten

Dec. 20, 1943

20 pg.

Comparison of Artificial and Motor Aging of Lube Oil. No satisfactory correlation could be found      Holten      July 19, 1944      10 pg.

Description of a Lubricating Oil Pilot Plant      2 pg.

Comparison of Lube Oils from Cracked Gasoline, Untreated and Alumina-treated      1 pg.

Effect of FeCl<sub>3</sub> in AlCl<sub>3</sub> in Lube Oil Synthesis      1 pg.

Aging Properties of Mixed Natural and Synthetic Lubes      1 pg.

Effect of Inhibitors on Aging Properties of Synthetic Oil      1 pg.

Clay Treatment of Synthetic Lube Treated with AlCl<sub>3</sub>      1 pg.

AlCl<sub>3</sub> Treatment of Lube Oil from Cracked Gasoline      1 pg.

Synthesis of 120 V.I. Lube from C<sub>6</sub>-C<sub>7</sub> and Higher Boiling Cracked Gasoline      1 pg.

Effect of AlCl<sub>3</sub> Concentration on Yield, Oil, and Contact Oil      1 pg.

Apparatus for Testing the Aging Properties of Lube Oils. Oil is aged for 6 hours under controlled conditions. Holten Mar. 3, 1944      2 pg.

Item 5 Analytical Methods for the Control of the Gasoline Synthesis

1) Investigation of gases: Sampling procedure; Orsat analysis; Orsat analysis with hydrocarbon circulation; nitrogen determination; oxygen determination; hydrogen sulfide determination; organic sulfur determination; organic sulfur detection; gasoline in tail gases; C<sub>2</sub>-C<sub>4</sub> in tail gases (activated charcoal absorption); olefins in tail gases; water in gases; heating value of gases (continuous and static colorimeter); density of gases; NO content of coke oven gas; detection of resin forming materials in gases; iron carbonyl in gases; ammonia in gases; cyanide in gases; acetylene in gases.

2) Analysis of the C<sub>2</sub>-C<sub>4</sub> fraction. Separation of hydrocarbons; gas density; heating value; C<sub>2</sub>-C<sub>4</sub> in tail; determination of CO<sub>2</sub>; determination of specific gravity in the liquid state; determination of the vapor pressure; determination of water content.

3) Coal, coke and ash analysis. Sampling; moisture content; ash content; coking yield; sulfur content (using a magnesia and soda mixture); nitrogen content; carbon, hydrogen and ash content; phosphorous content; heating value; specific gravity; porosity; ignition point; mechanical strength of coke; investigation of slag and ash; melting point of ash; determination of iron oxide and alumina.

4) Water analysis. Regular water analysis; determination of chlorine; determination of P<sub>2</sub>O<sub>5</sub>; determination of sulfur; determination of pH; determination of Al and Fe; determination of oil content; purity of distilled water.

5) Analysis of "Feinreinigungsmasse" (Na<sub>2</sub>CO<sub>3</sub>-FeO) organic sulfur removal. Activity; porosity; sulfide sulfur; total sulfur; sodium carbonate content; water content; bulk density.

6) Analysis of "Luxmasse" (FeO) H<sub>2</sub>S removal. Capacity for H<sub>2</sub>S; water content; sulfur content.

7) Analysis of activated charcoal. Water content; residual hydrocarbon content of charcoal; bulk density; adsorption efficiency for gasoline; adsorption efficiency for C<sub>2</sub>-C<sub>4</sub> fraction; wax content of charcoal; determination of activity.

8) Catalyst analysis. Catalyst activity; reduction value (portion of cobalt in metallic form); wax content of catalyst; sulfide sulfur and total sulfur; cobalt content; complete analysis (cobalt, total oxide, iron, thorium); bulk density.

9) Gasoline and heavier hydrocarbons. Distillation; olefins and aromatics (phosphorus pentoxide - H<sub>2</sub>SO<sub>4</sub>); specific gravity; iodine number (bromine and sodium bromide in methanol, and a special method using bromine, pyridine and H<sub>2</sub>SO<sub>4</sub> in glacial acetic acid and a N/10 solution of As<sub>2</sub>O<sub>3</sub>); aniline point; vapor pressure; neutralization and saponification number; octane number; flow and drop point (temperature at which the solid begins to flow and the one at which the first drop is formed); water determination (above 0.1% xylene is used and below 0.1% magnesium nitride (Mg<sub>3</sub>N<sub>2</sub>)); flash point; viscosity; pour point and melting point; gum content; induction period.

Holten

198 pg.

Item 5 Plans for Separation of C<sub>7</sub> Hydrocarbons

<u>Catalytic cracking plant flowsheet</u>	1 pg.
<u>Absorption, fractionation and stabilization section of catalytic cracking plant flowsheet</u>	1 pg.
<u>Complete workup of Fischer-Tropsch products (overall flowsheet)</u>	5 pg.
<u>Catalytic cracking plant flowsheet</u>	1 pg.
<u>Workup of Fischer-Tropsch products (diagrams)</u>	3 pg.
<u>Alkyl benzene (Kybol) pilot plant flowsheet</u>	1 pg.
<u>Workup of Fischer-Tropsch products (diagrams)</u>	2 pg.
<u>Catalytic cracking plant flowsheet (reactor arrangements)</u>	6 pg.
<u>Workup of Fischer-Tropsch products (diagrams)</u>	4 pg.
<u>Catalytic cracking plant flowsheet</u>	5 pg.
<u>Workup of Fischer-Tropsch products</u>	1 pg.
<u>Humidifier flowsheet</u>	1 pg.
<u>Time cycle diagram for toluene plant</u>	1 pg.
<u>C<sub>7</sub> polymerization plant flowsheet</u>	1 pg.
<u>Time cycle diagrams for toluene plant</u>	2 pg.
<u>Heptane separation plant (elevation and flowsheet)</u>	2 pg.
<u>McCabe-Thiele diagram (heptane-octane) and flowsheets</u>	11 pg.

Item 7 Synthetic Lube Oil for the German Army; draft of contract

Holten

3 pg.

Item 8 List of Japanese Patents on Lube Oil Synthesis

Holten

Oct. 18, 1940

3 pg.

Item 9 Proposal for the Addition of Synthetic waxes to Lube Oil  
The proposal made by an independent scientist was rejected by Ruhrchemie because the properties of the oil would suffer even though the oil would have better lubricating properties.

Holten

May, 1939

4 pg.

Item 10 Lubricating Oil from Fischer-Tropsch Products Obtained at Medium Pressure over Iron Catalyst. A gasoline fraction (70-180°C) high in olefins was polymerized with 5% AlCl<sub>3</sub>. A 115 V.I. oil of -46°C pour point was produced. Holten Feb. 4, 1941 2 pg.

Item 11 Properties of Lubricating Oil. Analysis of 2 synthetic lube samples and guaranties concerning properties and yields of lube for a license agreement. Holten 1937-1941 3 pg.

Item 12 List of Fischer-Tropsch patents given for various foreign licenses. Holten Jan. 28, 1939 2 pg.

Item 13 Alkylation of Fischer-Tropsch products, general discussion only. 2 pg.

Item 14 Ruhrchemie Patent Applications

Various aromatization applications: Covering use of vacuum; 30-50% chromoxide on magnesite; time cycle; use of alumina as carrier; use of chromoxide on alumina with Ni, Co, Th or Mn as activators; use of alumina of pH below 9; increasing temperature gradient through the reactor; reactor design; admixture of a heat storing material to the catalyst. 1938-1939 32 pg.

Two propane, butane dehydrogenation applications: Use of chromoxide on magnesite; use of chromoxide on alumina using Co or ThO<sub>2</sub> as activator 1938-1939 6 pg.

Catalytic cracking: High circulation rate of cracked products with cooler to remove heat of reaction; reduction of the hydrocarbon partial pressure with steam. 1939 12 pg.

Olefin polymerization: Thermal polymerization; phosphoric acid catalyst; continuous wetting of the catalyst with heavier oil, combination of vacuum cracking, catalytic polymerization and hydrogenation. 1936-1939 27 pg.

Item 15 Correspondence concerning Fischer-Tropsch Synthesis Using Gases from Electric Steel Furnaces

Holten

Feb. 16, 1942

12 pg.

Item 16 Proposal for a 25000 Tons/Year Synthesis Plant in Belgium  
Holten Sept. 24, 1942 12 pg.

Proposal for a 22,880 Tons/Year Synthesis Plant Using Iron  
Catalyst and Making Lube Oil Holten Aug. 16, 1943 7 pg.

Letter Concerning Proposed Hungarian Synthesis Plant  
Holten Aug. 9, 1943 2 pg.

Item 17 Technique for Determining Yields in Synthesis  
Holten Jan. 22, 1944 3 pg.

Item 18 Discussion Concerning the Hungarian (Pecheney) Synthesis Plant  
Project Holten Jan. 22, 1943 8 pg.

Item 19 List of Ruhrchemie Patents Covering Cobalt Catalyst, Iron Catalyst  
and Lube Oil Synthesis Holten Jan. 22, 1944 5 pg.

Item 20 Blends of Natural and Synthetic Lube Oil. It was found that natural  
lube addition improved the stability of the synthetic oil 4 pg.

Discussion concerning Hungarian Synthesis Plant (Pecheney)  
Holten Mar. 11, 1943 2 pg.

Item 21 Technical Data for a Proposed 25000 Tons/Year Synthesis Plant  
using Cobalt Catalyst; including a lube oil plant producing 6000 tons/year  
of oil Holten Feb. 28, 1943 6 pg.

Item 22 Pat. Appl. (I.G.) Treatment of Fischer-Tropsch products by Cracking  
where the charge is first catalytically dehydrogenated and isomerized at  
temperatures between 200 and 450° C. Feb. 25, 1939 5 pg.

Pat. Appl. (Ruhrchemie) Improvement of Fischer-Tropsch gasoline  
by first treating at 250-400°C with bleaching clay followed by the extraction  
of resin forming material at temperatures below 200°C with clay used in the  
first stage and subsequently extracted May 8, 1939 5 pg.

Item 23 Pat. Appl. (in Italian) Production of Synthesis Gas according to  
Hansgirk Apr. 28, 1939 3 pg.

Correspondence concerning the Hansgirk patent 1942 7 pg.

Item 24 Letter concerning Voltol May 25, 1942 2 pg.

Item 25 Alkylation of Benzene with Olefins over  $AlCl_3$  Catalyst. A  
partially unsaturated  $C_2-C_4$  fraction was used as olefin charge in one set  
of experiments. Using a propylene-butylene fraction it was found that the  
 $AlCl_3$  consumption was about 1 lb. per 40 lb. of resited propylene and  
butylene. 75% of the resited olefins were converted to the mono-alkyl  
benzene. Aug. 13, 1937 14 pg.

Item 26 Determination of Organic Sulfur in Gases by conversion in the  
presence of hydrogen and steam to  $H_2S$  over a glowing platinum 10 pg.

Item 27 Preparation of Synthesis Gas and of Acetylene by Partial Oxidation of Gaseous Hydrocarbons. Catalysts used included magnesia on sillimanite and on alumina where magnesia oxidized carbon formed, particularly by the alumina. Space velocities were primarily in the range of 500-1000 v/v/h.

I.  $\text{CH}_4 + \text{H}_2\text{O} \longrightarrow \text{CO} + 3\text{H}_2$ . Conversion was close to theoretical between 900 and 1100°C but fell off rapidly below 900°C particularly with sillimanite base catalyst.

II.  $\text{CH}_4 + \text{CO}_2 \longrightarrow 2\text{CO} + 2\text{H}_2$ . High carbon formation was noted between 1000 and 1200°C which could be reduced by increasing the CO<sub>2</sub> concentration. Below 900°C catalyst activity dropped off rapidly.

III.  $\text{CH}_4 + 1/2 \text{O}_2 \longrightarrow \text{CO} + 2\text{H}_2$ . Sillimanite base catalyst was used at 1000°C. Though conversions were high at higher space velocities, 500-1000 v/v/h was maintained to prevent acetylene formation.

IV.  $2\text{CH}_4 \longrightarrow \text{C}_2\text{H}_2 + 3\text{H}_2$  -92 Cal. This reaction goes, according to Pichler at temperatures above 1100°C, very short heating time, in the absence of large surface areas. A sillimanite tube without catalyst was used. The acetylene yield was highest (40%) at a CH<sub>4</sub>:O<sub>2</sub> ratio of 10:6. Temperature sensitivity appears negligible in the range of 1150-1300°C. Methane space velocities ranged from 10000-40000 v/v/hr. At a CH<sub>4</sub>:O<sub>2</sub> ratio of 2:1 carbon formation was excessive at 1270-1280° while it was negligible at 1250°C. Below 1150°C no carbon formation took place even at low oxygen concentration. It was also found that at constant temperature and increasing O<sub>2</sub>:CH<sub>4</sub> ratio (3:10 to 7:10) the quantity of methane converted to CO is always 1.5 times the amount of acetylene formed. This indicates that the combined reaction is  $5\text{CH}_4 + 3\text{O}_2 \longrightarrow \text{C}_2\text{H}_2 + 3\text{CO} + 6\text{H}_2 + 102 \text{ Cal.}$   
Holten Aug., 1931 27 pg.

Item 28 Engineering Drawing of a Synthesis Reactor 6 pg.

Item 29 Correspondence concerning the Preparation of Iron Catalyst  
1943 3 pg.

Item 30 Preparation of Sulfur-free Cobalt, Iron or Nickel by Electrolysis from a Formate Solution (Pat. Appl.) Letmathe, Apr. 7, 1943. 3 pg.

Item 31 Material Balance for Polymerization Plant Nov. 8, 1940 2 pg.

Item 32 Analysis of Waxes Extracted from Cobalt Catalyst for Iron and Cobalt 1 pg.

Item 33 Analytical Fractionation of C<sub>2</sub>-C<sub>4</sub> Cuts Similar to Podbielniak and Miscellaneous Analytical Methods 32 pg.

Item 34 Determination of Gasoline Remaining in Gas after Activated Charcoal Adsorption 5 pg.

Item 35 Determination of SO<sub>2</sub> in the Presence of H<sub>2</sub>S in Technical Gases 8 pg.

Item 36 Effect of Other Gases on the Absorption of Acetylene by Mercuric Cyanide 3 pg.



- Item 37 Determination of the Porosity of Material Used for Organic Sulfur Adsorption 2 pg.
- Item 38 Analysis of Various Waxes Wanne-Eickel July 19, 1939 2 pg.
- Item 39 Performance and Analyses of Adsorbents for the Removal of Organic Sulfur from Synthesis Gas Holten 1939-1944 11 pg.
- Item 40 Report on Exchange of Information of Fischer-Tropsch Licensees at Essen. The discussion includes high porosity adsorbents for organic sulfur, reactor design, mechanical stability of activated charcoal, corrosion problems and optimum method for catalyst regeneration.  
Essen Apr. 17, 1942 13 pg.
- Item 41 Fischer-Tropsch Plant for Belgium. Short description of a proposed 25000 tons/year plant using iron catalyst.  
Holten Nov. 19, 1942 2 pg.
- Item 42 Composition of Iron Catalysts found at the Ruhrchemie catalyst plant office. These notes give some methods of analysis and compositions at various stages in the preparation process. The catalyst contained iron, copper, calcium oxide, kieselguhr and potassium hydroxide. It was apparently prepared by several precipitations. Holten 7 pg.
- Item 43 Sketches of Various Sections of Fischer-Tropsch Plant. These include: product condensers, separators, manifolding of H<sub>2</sub>S removal equipment, water piping in CO to CO<sub>2</sub> conversion plant, flow through activated charcoal adsorbers, process piping for CO to CO<sub>2</sub> conversion, piping for drying extracted catalyst, piping for wax extraction from catalyst, design of H<sub>2</sub>S adsorbers. Holten 25 pg.
- Item 44 Operating Instructions for Fischer-Tropsch Plant include: startup of reactors; procedure for wax extraction from catalyst; hydrogenation of catalyst; use of plexiglass manometers.  
Holten 1939-1942 16 pg.
- Item 45 Cost of Preparing Catalyst for Removing Organic Sulfur from Synthesis Gas Holten 1944 4 pg.
- Item 46 Analysis of Dubbs Cracking Plant Products Holten, 1941 5 pg.
- Item 47 Performance of Two Cobalt Catalysts Holten, 1941-1942 2 pg.
- Item 48 Engineering drawings: Catalyst Plant (Elevation)  
Holten, Oct. 22, 1943 4 pg.  
Filter plant for drier Holten Sept. 10, 1943 4 pg.  
Flowsheet of Alumina Catalyst Plant Holten, July 7, 1943 4 pg.
- Item 49 List of Proposed Research Subjects. These include: Condensation of higher aldehydes, preparation of drying oils, removal of halogens from organic compounds. Holten Mar. 31, 1944 1 pg.

Item 50 Questions by and Answers to a Japanese Representative in  
Connection with Fischer-Tropsch Synthesis  
Holten Feb. 13, 1941 6 pg.

Item 51 Correspondence and Detailed Proposals by Lurgi for Japanese Lube  
Oil Plant from thermally cracked Fischer-Tropsch products boiling  
above 330°C (charge to cracker). The fractionation section consists  
of pressure distillation (slightly above atmospheric) to remove  
gasoline, vacuum distillation (about 100 mm. Hg.) to remove gas oil,  
and high vacuum distillation (3-5 mm. Hg.) taking spindle oil over in  
the first still and two lube oil fractions in the second still. Flow-  
sheet attached. Frankfurt May 22, 1941 30 pg.

Details of the polymerization and dechlorination mixing vessels.  
Holten Dec. 4, 1941 3 pg.

Correspondence concerning licensing agreement and yield, quality  
guarantees. 40% lube oil on a charge basis was guaranteed having a  
viscosity at 50°C of 8-22°E as desired, V.I. of 115-120° and a pour  
point of -25 to -40°C. 1939-1941 28 pg.

Miscellaneous correspondence concerning Japanese lube oil project  
Holten 1940 12 pg.

Description of the Ruhrchemie Lube Oil Process: Primary product boiling  
above 330°C from medium pressure synthesis is cracked thermally to produce  
83%w olefins. Either C<sub>6</sub><sup>+</sup> (67% of charge) or C<sub>5</sub><sup>+</sup> (73% of charge) are used  
for lube oil. Cracking is carried out under a vacuum in the presence of  
steam and with short residence time. 1-2% AlCl<sub>3</sub> are used for polymerization  
with temperature between 30 and 100°C depending on the viscosity oil  
desired. The crude polymer, containing 60% lube oil is dechlorinated by  
treatment with zinc oxide and clay followed by filtration. The dechlorinated  
oil is then fractionated as described above and bleached if desired. 22 pg.

Correspondence concerning the possible interference by Japanese  
patent 112265 of Standard Oil 5 pg.

Ruhrchemie A.G., Sterkrade-Holten

Bag 3439  
Target 30/5.01

Item 1 Index to Collection of Motor Test Curves 13 pg.

~~Item 2 Some of the Curves Listed in Item One 24 pg.~~

Item 3 Detailed Piping Drawing of Organic Sulfur Removal Equipment  
Dortmund Feb. 8, 1936 8 pg.

Item 4 Production Estimates, Properties and Cost Analysis for  
Switching from a Lube to Brightstock Production  
Holten 1942-1944 13 pg.

Item 5 Production Estimates and Costs for Aviation Gasoline  
Holten 1942-1944 4 pg.

- Item 6 Complete Cost Analysis for the Working of 61000 Tons of Fischer-Tropsch Primary Product Holten Sept. 10, 1946 6 pg.
- Item 7 Plot Plan, Building Numbers and Account Numbers for Toluene Plant Holten May 18, 1942 8 pg.
- Item 8 Research Suggestion to Investigate the Possibility of Carrying out the OXO Reaction on Nitrogen Compounds such as nitriles, isonitriles, etc. to produce glycols, aminoacids, etc. Holten Apr. 24, 1939 3 pg.

Item 9 Propionic Aldehyde from Ethylene via Oxo Process

Distribution of Products:

Propionic aldehyde	59%
Propylalcohol plus diethyl ketone	18%
Methyl ethyl acrolein	8%
Higher molecular weight products*	10%
Unidentified	5%
	<u>100%</u>

\* Probably produced by condensation of methyl ethyl acrolein during distillation and probably recoverable as the monomer by careful vacuum distillation. Holten Jan. 6, 1943 1 pg.

Monthly progress Reports for October and November, 1942. Suspension of catalyst in diesel fuel was used. Substituting water or a mixture of diesel fuel and water gave no reaction at all between 115 and 200°C. Two iron catalysts were tested: 100 Fe/10 Co/50 ThO<sub>2</sub> and 100 Fe/5 Cu/50 ThO<sub>2</sub>. Neither of them gave any conversion at temperatures between 115 and 185°C. The use of n-butylacetate for suspending the catalyst gave high conversion. The yield of propionic aldehyde was the same as when using diesel fuel or decalin.

Pilot Plant Run: Fin tube reactor containing 9 liters of commercial catalyst suspended in 40 Kg. diesel fuel. At 115°C and 150 atm. an ethylene-water gas mixture was charged at the rate of 18000 l./hr. Conversion was constant at 97.6% of ethylene charge during the two hours of the run. 18.6 Kg. of product were recovered containing 11.8 Kg. propionic aldehyde. 9 pg.

Flowsheet of propionic aldehyde plant without quantities Holten Dec. 16, 1942 2 pg.

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