

FILM STUDY GROUP
REPORT ON MICROFILM REEL NO. 27
Prepared by
SHELL DEVELOPMENT COMPANY

RESTRICTED -

Shell Development Co.
Emeryville, Calif.

This document contains information -1- affecting the national defense of the United States within the meaning of the Espionage Act, 50 U. S. C., 31 and 32 as amended. Its transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

Report on Roll 27 (Series A) of

U. S. Technical Oil Mission Microfilm

The material in Roll 27 represents technical papers seized at Ludwigshafen (I.G. Farben Ind.). It is for the most part not of general interest to the petroleum industry, and therefore, in preparing this report for the Petroleum Administration for War, no detailed translations have been made. All the items may be considered as of questionable value to the petroleum industry as a whole. There are, however, many sections that may be valuable to certain companies, especially those with strong chemical interests, and consequently value ratings have not been assigned to individual items. The more significant subjects in this roll include:

Catalysts for the manufacture of gases from coke or methane (B.S., B.Z., and brown oxide catalysts).

Catalyst for ammonia oxidation (N catalyst).

Hydrogen sulfide removal from gas with activated charcoal.

Industrial gas manufacture, especially H₂, CO, and mixtures.

Pimelic acid, preparation and uses.

Acetylenes, means of preventing explosions.

Distillation equipment for butadiene and styrene plants.

Propargyl alcohol, preparation and uses.

Chemical engineering investigations; new designs of fractionating columns, etc.

Patent applications on preparation of organic chemicals.

Drawings and flow sheets for plants making raw materials for synthetic rubber.

Abstracts covering Roll 27 follow. Most of the abstracts are intended only to furnish an idea of the contents of a section, and make no pretense of covering the possibly useful information. The abstracts are arranged in the same order as the items on the film.

Abstracts

Roll 27 of T.O.M. film
Bag 2169, Target 30/4.03 - Ludwigshafen

p. 4-104 Catalyst Manufacture and Properties.

p. 4-6 Availability of anhydrous sodium sulfide (sulfigran) for coal hydrogenation catalyst. 1943

~~p. 7-9 Life of Brown Oxide Catalyst.~~

The catalyst is used for the water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$). Life at a vapor hourly space velocity of 350-400 is 2-3 years. When it is necessary to change the catalyst because of increased pressure drop, the lower layer (flow downward) is replaced by fresh catalyst while the upper layer is replaced by used catalyst after this has been screened to remove fines. The rate of deactivation increases above 500°C. Oxygen and hydrogen sulfide in the charge also reduce the life as does a temporary cutting out of steam. Drops of water hitting the catalyst cause its disintegration. 1942

p. 10-18 Preparation of zirconium oxide gel from zirconium oxychloride and ethylene oxide, and production of pure chlorohydrin from the resultant aqueous ethylene chlorohydrin solution. Includes pertinent analytical methods. 1940

p. 19-28 Preparation of Tonalon (water-soluble alumina) from aluminum chloride and ethylene oxide. Also analytical methods and ethylene chlorohydrin recovery from aqueous solution. 1940

p. 29-46 Preparation of N-catalyst for the oxidation of ammonia with a air. This is a complete description of the manufacturing technique as well as of the analytical control methods. The composition is:

Fe ₂ O ₃	82%
Bi ₂ O ₃	6% min.
Mn ₂ O ₃	8% min.
Loss on ignition	3%
SO ₄ ⁼⁼	0.5% max.
Cl ⁻	0.02% max.
Cr	0

Particle size: 4 x 4 mm. cylinders
Weight: 980 grams per liter

1939

p. 47-57

Preparation of B.S. catalyst (judging by the evaluation test, it is used for the conversion of CO and H₂ to methane at 350°C.) This is a detailed description of the manufacturing technique and analytical control methods. Catalyst composition is given as:

Ni	24%
Mg	11%
H ₂ O	10%
SO ₄	0
NO ₃	0
Cl	0
Fe	0

Particle size: 5-25 mm.

Weight: 300 grams per liter

1939

p. 58-56

Preparation of B.Z. catalyst for the production of hydrogen from methane. This is a detailed description of the manufacturing technique and of the analytical control methods. The method of preparation follows. MgO, kaolin, and nickel carbonate paste (nickel content = 60% of total nickel) are well mixed with nickel nitrate solution (nickel content = 40% of total nickel). The mixture is dried and calcined at 500°C. The resulting calcined mass is ground, mixed with cement and water, and formed into rings or pellets with a press.

The composition of the calcined material is:

SiO ₂	33-33.5%
Al ₂ O ₃	11-11.5%
NiO	32-32.3%
MgO	18.1-18.4%
H ₂ O/120°C	0.7-0.8%
Ignition loss	2.0-3.5%
Cl	< 0.1%

50 pounds of this are mixed with 23 lbs. of alumina cement and about 6 quarts of water and pressed into rings 13 mm. high, 8 mm. I.D. and 3.5 mm. wall thickness.

1939

p. 70-97

Brown oxide, B.S., and B.Z. catalysts, plant at Frose.

This section includes a detailed cost analysis listing all major pieces of equipment, detailed plant layout drawings and flow diagrams, chemical requirements, and two drawings of a silica gel manufacturing plant.

1939

p. 98-104

Operating description of brown oxide catalyst manufacturing plant. This descriptor is in detail giving process as well as equipment information. Capacity of plant 150 metric tons per year.

The brown oxide catalyst consists of Fe_2O_3 and minor amounts of Cr_2O_3 . It is prepared by precipitating ferrous carbonate from ferrous sulfate solution with sodium carbonate, calcining the ferrous carbonate to ferric oxide, mixing the ferric oxide with chromium nitrate solution, to obtain a paste, pressing the paste into cakes, drying and calcining the cakes, and breaking into granules for use. 1940

p. 105-107 Formaldehyde production.

Brief report of an inspection of the Leuna plant where 350 tons/day of 30% formaldehyde are produced from methanol by oxidation with air and steam over a granular silver catalyst. With well purified methanol a yield of 80% (compared to 86% theoretical) is realized. 1943

p. 108-110 Vanol (glycol ethers) production.

Short note indicating that Vanol is produced from methylacetal with carbon monoxide and hydrogen over cobalt catalyst at 325 atmospheres. (Methylacetal is produced from formaldehyde). By-products include dimethylether. 1942

p. 111-159 H_2S absorption on activated charcoal (F-Kohle).

1940

This section contains primarily information on the removal of hydrogen sulfide from water gas by means of a special activated charcoal (F-Kohle). The process operates as follows: The gas which has been freed of tar and dust by means of coke filters or electrically, is passed through an adsorber filled with F-Kohle after addition of small amounts of air and ammonia. The catalytic action of the charcoal oxidizes the H_2S to free sulfur which is adsorbed on the charcoal. When the charcoal is saturated it is first washed with warm and cold water to remove salts and then with ammonium sulfide which dissolves the sulfur as polysulfide. Remaining ammonium sulfide is removed by steam and the charcoal is then ready for reuse. The steam, containing ammonia and hydrogen sulfide is condensed. After addition of sodium acid sulfide and calcium chloride solution the condensate is evaporated. The condensed overhead is pure ammonium sulfide for reuse and the bottom sludge contains impurities. The spent ammonium polysulfide solution is stripped in a column with steam at 10 psig. which keeps the temperature above the melting point of sulfur. The condensed overhead is ammonium sulfide solution while pure liquid sulfur is removed from the bottom. Operating results, cost analysis of the plant, description of the equipment, detailed flowsheets, and gas analyses are included. A subsequent letter discusses the possibility of carbonyl sulfide removal by adsorption with F and M charcoal and intermediate cooling and drying between the two adsorption stages. 1943

p. 160-173 Fischer-Tropsch Synthesis:

Includes letter requesting approval of an I.G. iron catalyst commercial plant giving expected product distribution (1943); summary letter on the status of experiments by various companies with iron catalyst to replace cobalt (1943); request for authorization for the construction of an experimental plant for liquid phase Fischer-Tropsch synthesis with oil circulation; description of liquid phase process with simplified flowsheet; discussion concerning the conversion of Fischer plants to the new catalyst.

p. 161-162

A letter from I.G. to Altpeter, Feb. 16, 1943. Iron catalyst gives yields of 145-150 g. total product per m³ of CO plus H₂. The product distribution is: C₃ plus C₄ (Gasol) 13-15% (80% olefins), gasoline to 175°C 32-35%, middle oil from 175 to 320°C 18-20%, light waxes boiling 320-400°C 10-12%, hard waxes 16-18%, alcohols (mostly ethyl) 5-6%. No operating details are given.

p. 163

A brief summary of the status of iron catalyst development work by Ruhrochemie, Brabag, Lurgi, I.G., and Rheinpreussen laboratories, February 16, 1943. Operating conditions generally used were: 200-260°C, 10 to 20 atm. pressure, feed 1.6 CO to 1.0 H₂. No details on catalysts. Yields and product distributions reported were similar to those obtained with cobalt catalysts. This summary is identical with that on p. 296 of Roll 26.

p. 169

Note concerning yields over fused iron catalyst with liquid product circulation. Temperature 230-240°C, pressure 25 atm., CO to H₂ ratio between 1.18 and 1.43. Catalyst load 0.72 kg. total product per liter of catalyst per day. Yield 150 g. total product per m³ of gas in two stages. Product distribution: gas 15% (80% olefins), gasoline 40% (O.N. 65, 50% olefins), middle oil 20% (C.N. 85, 50% olefins), wax 20% (m.p. 95°C, 50% olefins), alcohols 5% (C₁ to C₅).

p. 174-178

Cloudiness of ET 110 gasoline (isooctane) upon cooling to -60°C.
1944

p. 179-266

Manufacture of industrial gases:

Emergency measures for the temporary replacement of bomb-damaged gas holders at Oppau (4 pg. and 5 drawings), 1944

Data on the capacities of the Oppau gas plants at present and after completion (9 tables, 2 diagrams). 1943

Report on the cooler-saturator installation at the N-plant Oppau 63L.

(Conversion of hydrocarbon gases to CO and H₂ with O₂, and eventual further conversion of CO to CO₂). On the efficiency of using warm water from tail gas coolers for humidifying the incoming hydrocarbon gas and air (22 pg.). 1942

Conversion of carbon monoxide to carbon dioxide in gases containing phosphine (from carbide plants) over brown oxide catalyst. It was found that phosphine does not damage the catalyst (6 pg.).
1941

Report on plant operation for freeing an ammonia synthesis gas of methane by oxidation (9 pg.).
1942

Short description of pressure conversion plant No 315 for oxidizing CO to CO₂ for the production of a synthesis gas of proper CO:H₂ ratio (3 pg.).

Comparison of costs of three cases for the production of 97% hydrogen from water gas using different types of compressors and different pressures for the desulfurization and conversion steps (29 pg.).
1941

p. 267-280 Substances for gas proofing of textiles (patent applications);

- (a) Heat treatment of impregnated and coated fabrics
 - (b) Materials consisting of two layers of protective coating and a very smooth fabric layer in between.
 - (c) Fabric which is coated on one side with a protective material and on the other side with solvent-proof material.
 - (d) Use of fillers in the protective coating
 - (e) Use of plate-shaped fillers
- 1937

p. 281-285 Government orders for experimental work to be carried out by the I.G. (No technical data included);

Reaction of olefins with water gas in the presence of the sodium salt of sulfanilic acid.

Dehydrogenation of gaseous hydrocarbons over fixed bed catalyst, multiple stage process, with inter-heaters.

Preparation of synthetic fats from fatty acids from paraffin oxidation and synthetic glycerine, as well as physiological experiments on the nutritive value and physiological effect of these fats. Preparation of toluene from methylchloride and benzene.
1943

p. 286-287 Patent application for the preparation of aqueous emulsions of polyisobutylene by very rapid removal of the organic solvents.
1938

p. 288-292 Discussion of a process for the continuous production of Oppanol (rubber substitute, polyisobutylene) sheets. 1943

p. 293-294 Discussion of problems which may occur in air liquefaction plants if the air contains "Fog acid" (sulfur trioxide and chloro-sulfonic acid). Purification methods are considered. 1943

p. 295-304 Conference on the determination of olefins. The following methods were discussed:

- (1) Hydrogen number obtained with platinum catalyst. Aromatics are also hydrogenated by this method and deactivation of the catalyst with iron chloride or water to prevent aromatic hydrogenation could not be used since this also reduces the hydrogenation of di- and triisobutylene.
- (2) Leuna uses the Rhodan method for di- and triisobutylene.
- (3) A new low temperature bromine number at -50 to -80°C in methanol solution is discussed. At low temperature the oxidizing effect of bromine is reported to be smaller.

1941

p. 306-315 Drying with Silica Gel.

A descriptive report on the use of silica gel for air drying, maintaining low humidity, etc. 1939

p. 316-318 Experiments on the drying of liquids with silica gel which showed that liquids miscible with water cannot be dried at all, that partially miscible liquids can be partially dried and that liquids in which water is only very slightly soluble can be practically completely dried. 1938

Bag 2077, Target 30/4,03 I.G., Ludwigshafen

p. 5-13 Analytical methods.

p. 5-6 Procedure and calculations for the determination of carbonyl and acetyl numbers. 1944

p. 7-11 Determination of carbonyl groups in aldehydes and ketones by hot oxidation of the alcoholic solution containing free hydroxylamine and hydroxylamine hydrochloride; by reaction with silver nitrate. 1943

p. 12 Vapor pressure table for methylbutanediol-1, 4 (nearly illegible).

p. 13 Method for the determination of 1, 4 butanediol in crude solution. 1944

p. 14-15

Heats of combustion of some organic compounds.

<u>Compound</u>	<u>Q_p, kg-cal./mole</u>
Acrylonitrile	421.6
Methyl ester of acrylic acid	499.4
Butadiene	618.1
Cyclohexenenitrile	981.0
Methyl ester of cyclohexene- carboxylic acid	1069.0
Cyclohexene carboxylic acid	894.5
Pimelic acid	826.6
2-hydroxy-hexahydrobenzoic acid	879.1

Also heats of neutralization of the acids. 1943

p. 16-20

Methods of analysis of diisobutylene by bromination and hydrogenation (includes sketch of apparatus). 1940

p. 21

Vapor pressure of tetrahydrofuran in the presence of water and nickel carbonyl. 1941

p. 22-49

Preparation and utilization of pimelic acid.

p. 22-26

Letters indicating that the hexamethylene diamine ester of pimelic acid is of considerable value for the manufacture of bristles and silk substitutes. 1944

p. 27-28

Use of the ethyl hexanol ester of pimelic acid as a plasticizer and a comparison with the properties of the adipic acid ester. The pimelic ester has better dielectric and aging properties. 1944

p. 29-49

New processes for the preparation of pimelic acid. The process was developed because of the demand for super polyamides for synthetic fibers.

(a) Butadiene is condensed (Diels-Alder) with acrylonitrile or acrylic acid esters to cyclohexene derivatives. This compound is saponified to the sodium salt of the corresponding carboxylic acid which, upon heat treatment with 1.5 N NaOH solution, yields the sodium salt of pimelic acid and hydrogen. Yields and purity are excellent (92%).

(b) Variations of the same process: From butadiene and maleic anhydride, a tricarboxylic acid of 8 carbon atoms is obtained. Isoprene and acrylic esters yield beta and gamma methylpimelic acid. Butadiene and crotonic acid ester yield alpha methylpimelic acid as does piperylene and acrylic acid. Butadiene and cinnamic acid yield phenyl pimelic acid.

(o) Other processes for preparing pimelic acid: Action of caustic soda on hydroxy- and chlorohexahydrobenzoic acid. Report includes experimental data as well as a preliminary cost analysis. 1943

p. 50-87

Explosion Experiments with acetylene and mono- and divinylacetylene.

Safety measures have been developed to prevent explosion of the above compounds in commercial plants. These include:

- (a) grounding of all equipment;
- (b) elimination of copper acetylide (experiments are included on means to prevent its formation);
- (c) treatment of divinyl polymer peroxides with warm caustic to destroy them;
- (d) if the pressure is above 1.5 atm. the "Windkessel" (air chamber) of the pumps must be filled with 20 x 20 mm. iron Raschig rings;
- (e) methanol must be present in considerable proportion in the reboiler of monovinyl acetylene distillation;
- (f) a special, described, safety filter must be inserted into transfer lines; etc. Many experiments are described in detail. 1939

p. 88-98

Theoretical aspects of Acetylene decomposition. Effect of inside diameter and wall thickness of pipes on the propagation of decomposition waves. Thin walled pipes of small diameter are most desirable. 1941

p. 99-119

Acetylene decomposition experiments.

It was found that a combination of wire mesh filters and bundles of small tubes are adequate protection against explosion in pipes for a butadiene plant at 100 atms. pressure. 1941

p. 120-153

Descriptive report of the continuous distillation section of the commercial plant at Schkopon for the production of butadiene, ethyl benzene, and styrene. This includes a description of the equipment, layout, construction details, many photographs, details of bubble tray design. 1940

p. 164-163

Removal of 0.025% Silicic acid from aqueous crude butynediol solution. Freshly precipitated magnesium hydroxide as well as milk of lime are satisfactory. 1944

p. 164-171

Preparation and utilization of propargyl alcohol. This product has good rust removing properties but does not prevent subsequent rust formation. Methods for the conversion of propargyl alcohol to allyl alcohol are discussed. 1942-1944

p. 172-203 Chemical Engineering Investigations. (Very brief outlines of tests and developments.)

p. 172-180 (a) Fractionation: a number of new bubble tray designs are discussed both for commercial and laboratory columns for the purpose of increasing tray efficiency and decreasing the necessary tray spacing. Sketches are included. 1942

p. 181-190 (b) Drying and evaporation. Different types of dryers, including spray dryers, grooved rollers, vacuum, Buttner dryers, etc. 1941

p. 191-198 (c) Filtration, evaporators, gas burners, etc. 1940

p. 199-203 (d) Heat transfer, etc. 1939

p. 204-226 Preparation of organic chemicals.

(a) Patent application for the production of delta 3-tetrahydrobenzoic acid from butadiene and its homologs with alpha and beta unsaturated carboxylic acid nitriles in the presence of emulsion inhibiting additives and in the absence of air, at 100°C. 1944

(b) Patent application for the preparation of salts of hydroxycarboxylic acids from diols with non-adjacent hydroxyl groups by treatment at elevated temperature with alkali- and alkali earth hydroxides. 1944

p. 209-214 (c) Discussion of use of residual butadiene from polymerization by Diels-Alder synthesis, in place of the present recovery by azeotropic distillation. Production of Bunol (polymerization in the presence of Na or K and 10% toluene without interference from butylenes, to leather oil), Pervinan (by Buna 32 polymerization), and butane tetracarboxylic acid (by addition of maleic acid and treatment with nitric acid). 1944

(d) Patent Application on preparation of hydroxycarboxylic acids from diols in the presence of alkali or alkaline earth hydroxides. 1944

(e) Preparation of nitriles from butene diol, cuprous cyanide, and hydrochloric acid. 1942

(f) Patent application for the preparation of carboxylic acids by treating aliphatic and cycloaliphatic dihydroxy compounds of at least three carbon atoms with alkali or alkali earths at elevated temperature and possibly in the presence of diluents. 1943

(g) Patent application for the preparation of carboxylic acids by treating six membered cyclic olefins containing an active group, preferably in the alpha position, with alkali or alkali earth-materials. 1943.

p. 227-268 Drawings on the manufacture of chemicals for synthetic rubber,

Tetrahydrofuran

(Drawing No.)

page 229	L-15175a-2	Tetrahydrofuran Distillation
230	L-6119b-1	Tetrahydrofuran Reactors
231	L-6120b-1	Tetrahydrofuran Reactors

Ethylbenzene Styrene

233	L-15606a-2	Alkylation
234	L-15607a-2	Alkylation
235	L-6083a-2	Benzene-Ethylbenzene Distillation
236	L-5884a-1	Ethyl Benzene Dehydrogenation
237	L-4225c-1	Styrene Distillation
238	L-14407b-2	Styrene Distillation
239		

Butane-diol Distillation

241	L-15715-2	Material Balance
242	L-5202a-1	Apparatus
243	Anl9a	Flowsheet
244	L-5707	Apparatus and Piping
245	L-5204a-1	Building

Butynediol Distillation

247	L-13471f-2	Flowsheet - one reactor cell
248	L-5769d-1	Reaction chamber
249	L-4118a-1	Degasification column
250	L-5167e-1	Degasification Flowsheet
251	L-5481e-1	Acetylene Pumps
252	L-5861e-1	Piping-Elmo chamber
253	L-6328b-8	Flowsheet-acetylene residue gas wash
254	Lu-128	Material balance
255	IN 22e	Flow diagram
256	IN 25a	Detail flowsheet
257	L-5201d-1	Flowsheet
258	L-5675f-1	Tankage
259	SK 2/1/45	New flowsheet
260		New plot plan
261	L-13532b-2	Plot Plan
262	L-5167c-1	Degasification

Aldol Condensation of Acetaldehyde

(Drawing No.)

page 264	L-5942a-1	Flowsheet
265	L-5943a-1	Reactors
266	L-5944a-1	Distillation
267	L-5052b-1	Piping
268	N-12280C-2	Flowsheet (proposal)

FK, HHV/fad