

**FILM STUDY GROUP**  
**REPORT ON MICROFILM REEL NO. 26**  
**Prepared by**  
**SHELL DEVELOPMENT COMPANY**

# SHELL DEVELOPMENT COMPANY

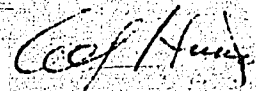
DATE November 13, 1945

TO SHELL DEVELOPMENT COMPANY, SAN FRANCISCO  
 FROM SHELL DEVELOPMENT COMPANY, EMERYVILLE  
 SUBJECT U. S. TECHNICAL OIL MISSION, MICROFILM ROLLS 26 AND 27

Attached are reports on Rolls 26 and 27 (Series A) of the Technical Oil Mission microfilm, as requested in your letter of October 3. These reports have been prepared with the interests of the Petroleum Administration for War in mind, according to the directions in Mr. Miller's letter to you dated August 9. We are returning the microfilm rolls under separate cover.

Some of the material in these films may be of considerable interest to the chemical industry, but there is relatively little that is of general value to the petroleum industry. For this reason we have restricted our reports to rather brief abstracts, except for a translation covering butane dehydrogenation. Although the bulk of the material might be classified as of questionable value from P.A.W.'s standpoint, we have preferred not to assign individual classifications because of the difficulty in deciding what might be of value to certain companies.

The reports on Rolls 26 and 27 commence with brief summaries and assessments, and continue with the individual abstracts, which are in the same order as the items on the films. The detailed page references will facilitate location of any particular subject by interested persons.



W. J. Hund

HHV

HHV/fad

Attach: Report on Roll 26  
 Report on Roll 27

cc: (with attach)

- 10 - Shell Development Co., S. F., Attn. Mr. Westermann
- 1 - Shell Development Co., S. F., Attn. Mr. F. Kunreuther

RESTRICTED -

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Shell Development Co.  
Emeryville, Calif.  
Nov. 18, 1945.

Report on Roll 26 (Series A) of

U. S. Technical Oil Mission Microfilm.

The material in Roll 26 represents technical papers seized at Ludwigshafen (I.G. Farben Ind.), and covers a considerable amount of chemical synthesis work as well as some information on hydrocarbon reactions. Most of it will be of minor interest to the petroleum industry as a whole. In preparing this report for the Petroleum Administration for War, translation has been made only of a section on butane dehydrogenation, while abstracts have been given for the remaining material. No value ratings have been assigned to individual items, since it is felt that many of them, not of direct interest to all refiners, will still be of great interest to companies doing chemical work.

Some of the more significant subjects in Roll 26 are:

Gasification of coke with oxygen and steam.

Acetylene chemistry, a review of new reactions.

N<sub>2</sub>O ("GM<sub>1</sub>") as an antiknock for aviation engines.

Alkylate production, including butane isomerization, catalytic dehydrogenation of butane, and sulfuric acid alkylation.

Polymerization of olefins.

Butane dehydrogenation by alternative processes such as chlorination followed by dehydrochlorination.

Propane dehydrogenation, plant design.

Fischer-Tropsch synthesis of hydrocarbons, including use of iron catalyst, liquid phase operation, oil recycle operation, hot gas recycle for heat removal production of wax, and theory of heat transfer.

Synthesis of fatty acids from CO and olefins.

Synthetic lubricating oils by polymerization of olefins from the cracking of wax.

Evaluation of waxes as stocks for preparation of lubricating oils by cracking and polymerization.

Aviation fuel ingredient ("Peroptan") from isobutane and propyl chloride.

Combustible tablets to aid in starting Diesel motors at low temperatures.

A few comments may be made on those subjects in the above list that are of particular interest to the oil industry.

The gas N<sub>2</sub>O is a fairly effective antiknock agent but it does not appear to have much if any advantage for American use. It requires special equipment for handling and injection.

Alkylate production in Germany followed known methods. Butane was isomerized in vapor phase over solid aluminum chloride, and the isobutane was alkylated in the presence of sulfuric acid with butylenes obtained by catalytic dehydrogenation of butanes over chromia-alumina catalyst. The development of the processes apparently had not reached the same high degree found in the United States, except possibly for the butane dehydrogenation which was conducted in a somewhat novel manner over a moving bed of spherical catalyst. Polymerization of olefins likewise was not especially different, although there is an indication that a high-pressure operation with a magnesium phosphate catalyst may have given somewhat higher octane number for the hydrogenated product than the usual polymerization.

Fischer-Tropsch studies included in this film were chiefly directed toward finding iron catalysts to substitute for the scarce cobalt, but there is also much other information of possible value.

The synthesis of lubricating oils by polymerization of olefins from the cracking of n-paraffin waxes is already known in this country, although economic reasons restrict its use.

A purported synthesis of triptane ("Peroptan") from isobutane and propyl chloride in the presence of aluminum chloride appears to be novel. It actually gave a product much like isooctane. This process was being actively studied near the close of the war, but did not come into large scale use. The exact operating conditions are not given in Roll 26.

Abstracts covering Roll 26 follow. Most of the abstracts are intended only to furnish an idea of the contents of a section, and do not present all the possibly useful information. The abstracts are arranged in the same order as the items on the film.

<u>Abstracts</u>	
Roll 26 of T.O.M. film	
Bag 2463, Target 30/4.03 I. G., Ludwigshafen	
p. 1-8	<u>Ketone Peroxide.</u> 1942

An outline of properties of ketone peroxides recovered from oxidation of paraffins, in particular di-n-propyl ketone peroxide and butanone peroxide. Ten per cent of the former in Diesel oil of

86 C.N. increased the C.N. to 160. Considerable discussion on the danger of explosion in the use of such additives. The quantities available were apparently not large.

p. 9-16 Gasification Experiments.

May, 1941

Continuous gasification of coke with oxygen and steam. Some analyses of charge and product as well as yield data. A gas containing 22% CO<sub>2</sub>, 35% CO, and 40% H<sub>2</sub> was obtained. Utility consumptions, etc.

p. 17-43 Acetylene Chemistry.

Nov. 1941

General review of the production methods for acetylene and products derived from it including: butadiene, cyclooctatetraene, vinyl ether (with alcohol), plastics (with phenol) vinyl amines (with amines), alkynols and diols (with aldehydes), acrylic compounds via cyclopropanone.

The report includes the catalysts used as well as methods for producing derivatives and their use, but does not give detailed data.

p. 44-52 Chlorination Reactions. (Flow diagrams) Only one dated, Aug. 12, 1942

Very simplified flowsheets for: oxidation of HCl and the recovery of Cl<sub>2</sub> by absorption in sulfur chloride, butadiene from dichlorobutane, chlorination of paraffins for production of isopropyl ether, isobutylene and butadiene, paraffin dehydrogenation via chlorination, and (p. 52) an overall flow, with quantities, for the processing of isobutane by chlorination, dehydrochlorination, polymerization, and hydrogenation to produce isooctane. The HCl was converted to Cl<sub>2</sub>, which was separated with sulfur monochloride and reused.

p. 53-139 Gl<sub>2</sub> (N<sub>2</sub>O) for Aviation Engines.

1941

This section deals with work on the detonation inhibitor N<sub>2</sub>O and is concerned primarily with methods of injecting the material into the engine, problems in connection with insulating the N<sub>2</sub>O containers, production problems, flight test results, explosion hazard experiments (very extensive with photographs, etc.). The addition of 100 g. N<sub>2</sub>O per horsepower-hour increased the power output of an aircraft engine from 690 to 1000 H.P.

p. 140-141 Production Costs, Heydebreek

April, 1943

A table giving production capacities and various allocated costs for products made at Heydebreek, taken from a report to the head of the I.G.

207  
277

p. 142-153 Technical data on the AT 244 process (Butane dehydrogenation, butane isomerization, and alkylation). This report includes information on plant capacity, equipment requirements, process description, cost analysis, isomerization plant flowsheet with operating conditions and material balance, operating data and list of equipment. The Leuna plant had a capacity of 70,000 tons alkylate/year by this process. Butane dehydrogenation was effected over a slowly moving bed (2 to 3 hours holding time in the externally heated, 3 inch O.D. tubes) of spherical catalyst at about 550°C. Brief description of plant and operation. A conversion of 20% and an ultimate yield of 85% were reported. See also p. 159, below. June, 1942.

p. 143-145 Butane Dehydrogenation (translation)

Technical basis for evaluation of the AT 244 Process, from the discussions in Leuna on June 8 to 10, 1942. Dated June 25, 1942, at Oppau.

Participants: From Leuna: O. I. Keinke, Dr. Kading, Dr. Orlicek, Dr. Schmidt (part time), Dr. Fischer (part time), Ing. Weith (part time),  
From Oppau: O. I. Giehne, D. I. Schröder, Dr. Hegelmann.

A record of the results of the discussion has been prepared in Leuna. The following notes give some of the basic technical data.

Dehydrogenation. The liquid butane is vaporized in two vaporizers at about 3 atm. pressure, and is lead to the reactor ("ofen") through heat exchangers and a final preheater ("Spitzenvorwärmer"). The vaporizers are equipped with dip-tubes, so that increasing pressure in the vaporizer lowers the liquid level and diminishes the heating surface. The Leuna reactors (five reactors plus two in reserve) are ready for operation with a capacity of 70-80,000 tons of alkylate per year (about 1700 B/D). Because of the tight gas supply only one reactor is operating at present, and this, according to "Obering" Keinke has been going ten days with 85% yield.

Output: One reactor produces 6,500 tons/year of olefin, corresponding to 14,000 tons/year of alkylate.

For Blochhammer three plus one reactors will thus be necessary. The construction department of Leuna counts on 20% conversion.

Yields in the laboratory are 90-93%.

At the start yields of 60-65% were got in plant reactors. Now it is certainly possible to reach over 82%, 85% can practically be counted on, and there are hopes of going higher.

Construction: One reactor consists of 8 bundles, each with 16 tubes of 76 mm. O.D. and 3 mm. wall thickness. Each catalyst tube has its own lock ("Schleuse", probably a slide valve). In the heating-gas space of each bundle there is a central filler ("Verdränger") to increase the gas velocity. Each group of 16 tubes is actuated by a gear rim placed in the vapor space. It proved to be very important to protect this rim gear from catalyst dust to avoid abrasion of the gear. Therefore a small stream of flushing butane was led in. The control of catalyst flow under each catalyst tube is done with tuning forks ("Stimmgabeln"); the lock bunkers are controlled with selenium cells.

Each reactor has three bundle preheaters of 197 m<sup>2</sup> each; two of these are of steel ("Schmiedeeisen") and the third of "Sichromal". Then comes a final preheater of 50 m<sup>2</sup> which heats to 490-550° (now 500°). The outer dimensions of the reactor furnace are: diameter, top 4.4 m., bottom 5 m.; height, without bunkers, 6.25 m.

The flue gases at about 650° serve to preheat butane in the final heater and also to preheat air. The furnace efficiency is 68 to 72%.

It is remarkable that the spherical catalyst tends to bridge and jam when the ratio of the catalyst diameter to the tube diameter exceeds 1:10. Too large a catalyst size must therefore be avoided.

The operation is not directly controlled according to the temperature; it has proved more reliable to go by the gas density.

The catalyst is in the reactor 2.5 hours at reaction temperature. The lock time ("Schleuszeit") is 2.5 to 6 hours. The durability of the catalyst was stated to be 300 to 500 hours, in January, 1942.

The catalyst regeneration is made in a regeneration furnace at 400-450°C. The catalyst in a ring-shaped shaft is traversed radially by nitrogen and 2% oxygen from a circulating blower. One regenerator serves two to three reactors.

To purify the hot, dehydrogenated gas from catalyst dust, carbon, etc., water is sprayed into the exit gas line at about 180° gas temperature, and the gas, at present, at 70-80° is led into a filtering arrangement with filter sacks. Leuna believes the filter installation could be replaced in future plants by an oil scrubbing tower.

The very extensive measuring and regulating arrangement has, according to the plant people (Dr. Fischer), worked out very well so far.

Condensation and oil scrubbing: To separate the resultant hydrogen and methane, the gas is compressed in three vertical compressors, each 3430 m<sup>3</sup>/hour. The C<sub>4</sub> fraction is condensed with water cooling. The compression is to 10 atm. because the compressors were available for this pressure, but a lower pressure would suffice.

It has proved to be advantageous to aftercool the gas with brine to 5-6°, before the oil scrubbing. The temperature limit is set by the formation of gas hydrates, as otherwise solid formation would occur. The cooled gas then passes at 9 atm. through the oil scrubber to further free the hydrogen from C<sub>4</sub>. The oil scrubbers consist of one plus one tube bundles, each with 55 tubes of 100 mm. diameter which are filled with 15 mm. Raschig rings. The oil is lead through a spider over the packing in the tubes, which are cooled outside by 25% methanol solution to 5°C.

After the fat oil has been heated in one plus one heaters with high pressure steam, depressuring and degasification follow in one plus one desorption towers of about 1 m. diameter. The oil circulation is 8 to 16 m<sup>3</sup>/hour, depending on the load.

(The notes continue with isomerization, etc.)

p. 154-178 Minutes of a discussion of work at Leuna, Oppau, and Ludwigshafen on the AT 244 process (see above).

Meeting on March 16-17, 1942  
Notes-Apr. 10, 1942 and Aug. 1942

(157, 158) The status of testing of butane dehydrogenation catalysts is given. Older catalysts were 967K and T9. Cooperative work to be done is outlined.

(159-165) Butane Dehydrogenation (translation)

The dehydrogenation of i-butane (Leuna) D. I. Weidmann

Present status of the plant: The equipment has been developed to the point where the necessary number of reactors can be considered ready for operation. The difficulties experienced at the start (tube ruptures, weld failures, bridging of catalyst in tubes, and foreign bodies in the catalyst) have not occurred recently. On-stream periods of sixty days without interruptions have been reached. The aim is 100 days of operation between shutdowns. The material injuries experienced at Scholven with material FF-30 have been avoided at Leuna by the use of Sichromal 8. The locks ("Sohläusen") can now be considered dependable for operation.

Reactors (four in plant) are each fed with 1500 N m<sup>3</sup>/hour of isobutane at a space velocity of 1000. The isobutane content of the feed is 85-88%. Conversions of 18-20% with a yield of 80% are obtained. Light bridgings of the catalyst occur occasionally; reasons for this are being examined at present. The cycle gas enters the top of the oven at 780-800°C and leaves the end of the tube bundle at 615-630°C.

The residence time of catalyst 5063 in the dehydrogenation reactors is 2-3 hours, and its life is 500-600 hours. Catalyst attrition is more rapid than the decline in activity. Specific consumption rates are not yet available.



Dehydrogenation of n-butane (Leuna) Dr. Nowotny

Two catalysts have been developed for normal butane dehydrogenation in Leuna, catalyst 5530 prepared from alumina ("Aluminattonerde") unpeptized, and catalyst 3675 prepared from alumina ("Aluminattonerde") peptized with nitric acid. Both catalysts were prepared in a kneader, and contained 10% Cr<sub>2</sub>O<sub>3</sub> and 2% K<sub>2</sub>O. Catalyst 5530 can now be manufactured on large scale, but the production development of catalyst 3675 still continues. (aluminattonerde is alumina ppt. from sodium aluminate - tr.)

Status of laboratory researches.

In a laboratory reactor with 14 mm. diameter and 25 cm<sup>3</sup> catalyst volume the following results were obtained at a space velocity of 1000 during a period of 400 dehydrogenation hours.

<u>Catalyst</u> <u>%</u>	<u>Conversion</u> <u>%</u>	<u>Yield</u> <u>%</u>	<u>Carbon deposit, % based on</u> <u>n-butane converted</u>
5530	30	88-90	1-1.2
3675	33	92-94	1

The initial temperature with both catalysts was 520°C. After 30-60 dehydrogenation hours the temperature of catalyst 5530 had to be raised to over 560°C to maintain a 30% conversion. Catalyst 3675, however, did not require a temperature elevation to above 560°C until 300 hours had passed, which had a favorable influence on yield.

Status of pilot plant researches.

In a pilot plant reactor (60 mm. tube, gas heated) a conversion of 25-27% with a yield of 81-82% was obtained when operating with catalyst 5530 at a space velocity of 650-700. Catalyst attrition was very low and amounted to only 0.2% per passage ("Schleusing"). The catalyst had a life of about 300 hours, and yielded 160-170 kg. of butylene per kg.

For full scale operation with catalyst 5530 a conversion of 25% and a yield of 80% are estimated, at space velocity of 650; for catalyst 3675 a conversion of 25% and a yield of 85-88% at a space velocity of 800.

Composition of product butylenes.

In order to determine the content of alpha and beta butylenes in the butylene produced by dehydrogenation, the butylenes were washed out with silver nitrate after driving off the lighter fractions. A distillation of the resulting pure butylenes in a low temperature column according to Koch and Hilbarath indicated 43% alpha and 57% beta butylene. This composition of the product butylenes proved to be independent of the dehydrogenation temperature. These values agree approximately with values calculated from the theoretical equilibria.

Dehydrogenation of n-butane (Oppau)

Dr. Conrad

At the conclusion of the hydrocarbon discussions in Leuna on 29-30 of February, 1941, (sic) the production of spherical catalyst particles from the active alumina of Oppau by means of Leuna's ball machine ("Frankoma") was undertaken. From Oppau's chromia-alumina paste spherical particles could be formed without difficulty, but from pure alumina paste no spheres could be obtained because of the soapiness. By peptizing with aluminum nitrate it was finally possible to prepare an alumina paste which could be processed by the Leuna-forming machine. The resultant catalyst from these studies, prepared by impregnating with chromium and alkali, carries the Oppau designation K-445.

A usable spherical catalyst (967-K) has resulted from further studies by Dr. Drexler with the Stbwener centrifugal tube method. One-hundred and fifty more liters of this are to be sent to Leuna.

Catalyst balls from Oppau active alumina prepared in a marble factory were hard and very good catalytically, but cracked suddenly after 2-3 operating periods.

Attempts to press unpeptized alumina with the Kilian press into approximate spheres led after overcoming various difficulties to a truly useful catalyst (T-9), of which a larger charge is to be made up in the near future. In small scale tests it was found that this catalyst flowed well ("liess sich gut schleusen"). It is understood that 250 liters of this catalyst are to be sent to Leuna for testing.

According to a communication from Dr. Langheinrich, Leuna will discontinue the impregnation of alumina and like Oppau will work up a chromia-alumina paste.

Comparative testing of various catalysts in the laboratory for n-butane dehydrogenation under the following conditions:

- Reactor diameter, 30 mm.
- Length of catalyst bed, 70 mm.
- Space velocity, 1000.
- Temperature 510°C, rising to 580°C.
- Operating period, 5 hours.

gave the following average results for four operating periods

Catalyst	Strength kg. <sup>+</sup>	Loose density gr./l.	% C <sub>4</sub> H <sub>8</sub> in product gas	Conversion vol. % C <sub>4</sub> H <sub>8</sub> based on feed C <sub>4</sub> H <sub>10</sub>	% C on catalyst, based on C <sub>2</sub> H <sub>6</sub> obtained
Leuna 5063	29	798	14.1	17.5	1.5
Leuna <del>5530/</del> S 18	<del>25</del>	<del>948</del>	<del>17.3</del>	<del>22.5</del>	<del>1.8</del>
K 445	21	690	18.5	25	1.9
T 9	30 <sup>++</sup>	848	18.7	25	1.3

Under conditions which were not wholly comparable, Leuna (Dr. Nowotny) obtained the following results with catalyst 3675, at a space velocity of 1000, a four hour operating period, and after 25 regenerations:

Leuna 3675	20	---	20.5-22	28.5	1.0
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Oppau and Leuna have both established that on increasing the chromium content of a catalyst the carbon deposition on the catalyst increases.

<sup>+</sup> Crushing strength is no measure of stability in slufcing ("Schleusfestigkeit").

<sup>++</sup> Pressed on flat side.

#### Dehydrogenation of n-butane with gas recycling. Dr. Donath

At the instigation of Herr Dr. Pler other methods of butane dehydrogenation besides those used commercially at present are to be investigated. Dehydrogenation by means of powdered catalyst appears promising as does also dehydrogenation over a fixed catalyst with gas recycling. Regarding dehydrogenation with powdered catalyst let it simply be said that, in the use of a powdered catalyst by Dr. Conrad for treatment of n-butane, initially very promising results were obtained (40% conversion and a yield of 88% butylene). In the following, however, only studies with fixed catalyst will be described.

The procedure depends upon supplying the negative reaction heat by heating and recycling the reaction gases. The investigations were carried out with one liter of catalyst in a reactor equipped

with a circulating blower. The blower had a capacity of about  $10 \text{ m}^3/\text{hour}$ . The recycled gases were heated on the outer walls and then passed again through the catalyst. The catalyst bed had a diameter of 150 mm. and a length of 60 mm. The equipment was made of  $\text{V}_2\text{A}$ . An alumina-potassium dichromate catalyst in the form of 4 to 8 mm. granules was used, which in activity corresponded to that supplied by Dr. Conrad.

The results obtained are collected in the following table, and for comparison results obtained with the same catalyst in an externally heated 100 cc. reactor without gas recycling are given.

	<u>With gas recycling</u>	<u>Without gas recycling</u>
Reactor size, $\text{cm}^3$	1000	100
Liters butane recycled/liter fresh butane	40	0
Temperature, $^\circ\text{C}$	530	535
Throughput, liters n-butane/l. catalyst/hour	250	500
Conversion, %	35	35
Selectivity, %	94	94

With recycling and half the throughput the same conversion and selectivity were obtained as without recycling. For regeneration of the catalyst the apparatus was flushed with nitrogen, and with the recycle blower running, air was added. Removal of the combustion heat was effected also by the recycling. Danger of a scaling of the preheater and blower need not exist because the oxygen addition can be made directly before the catalyst, and the regeneration stopped when the oxygen begins to come through (black core regeneration).

A calculation of the technical relationships, especially of the pressure drop, shows that with presently available equipment (for example, circulating blowers for hydrogenation preheaters) the reaction can be accomplished on a large scale without the necessity of developing new machines.

#### Preparation of dehydrogenation catalyst Dr. V. Fúner

The high pressure laboratories in cooperation with Leuna are arranging for a plant in Oppau 802 for the manufacture of spherical catalyst from active alumina. The construction is to start in the middle of 1943. On the grounds of dependability, the manufacture will follow the procedure developed in Leuna, without changes. The active alumina will be obtained from Oppau (Dr. Drexler). Initial difficulties, which were encountered in the forming at Leuna at the start of the development, have now been completely overcome.

Herr Dr. Wietzel suggested that, in case the Ammonia Laboratory should succeed in forming spheres of alumina by a simpler process (forming in Killian press or by spinning in a tube), the manufacture of the catalyst should be done by the Ammonia Laboratories. On the question of the subsequent impregnation of the catalyst after forming into spheres, Herr Dr. Drexler remarked that the chalky alumina recently developed in Oppau could be more evenly impregnated than the only earlier, grainy, modification of alumina.

Dehydrogenation of n-butane by the chlorination procedure. Dr. Bähr

Since 1937 there has been operating in Leuna a large pilot plant for the production of butadiene, and also of butylene, from n-butane by the chlorination-dehydrogenation procedure. The dehydrogenation is effected at 400-600°C. The HCl evolved is washed out with 20% hydrochloric acid. Then the HCl is driven off from the 36% efflux acid by distillation, and is converted to chlorine by the Deacon process over a copper catalyst. Later, in cooperation with Bitterfeld, a more economical and reliable recovery of the chlorine was carried out by electrolytic splitting of the 36% hydrochloric acid into chlorine, hydrogen, and 15-20% hydrochloric acid.

In Ludwigshafen experiments with propane and n-butane were carried out, in equipment that gave 10 kg. of butylene per hour at a conversion of 50%.

From 100 parts of butane there were obtained:  
 70 parts butylene (95-98%)  
 25 " butadiene (98-100%)  
 5 " higher chlorides.

A calculation of the process based on butane at 0.25 RM/kg., and electricity at 0.02 RM/kWh, gave costs of 0.80 RM/kg. of butadiene, and 0.46 RM/kg. of butylene. The installation cost per yearly ton of butylene, computed without consideration of the by-product butadiene, amounts to 500 RM. A third of the working costs are the electrical costs.

(The notes continue with concentration of butylene by a silver nitrate wash).

(p.165) Butylene concentration with silver nitrate.

Laboratory results using saturated silver nitrate solution for extraction of a butane-butylene mixture.

(p. 166) Vapor phase isomerization of n-butane over AlCl<sub>3</sub>.

A layer of AlCl<sub>3</sub> lumps above a supporting packing was used. Conversion 30%, loss to C<sub>3</sub>, 2%. Catalyst life 140 to 200 pounds isobutane per pound of catalyst. It was found that the presence of iron in the AlCl<sub>3</sub> considerably increased activity.

(p. 166-173) Alkylation.

Description of laboratory apparatus and test results on sulfuric acid alkylation of butene-1, butene-1-polymer, diisobutylene, propylene, propylene polymer, and polymer from Fischer-Tropsch synthesis gas. No advance over American practice. Also a short report on boron fluoride-HF alkylation of propylene with isobutane.

(p. 174-178) Polymer. (propylene-butylene, vapor phase).

Operation at 3,000 psi. and 750 psi. Using the "high pressure carbon catalyst", phosphoric acid was washed off, leading to corrosion difficulties. The "medium pressure carbon catalyst" was considerably more successful. Large scale tests are planned with magnesium phosphate catalyst at 3,000 psi. The behavior appears to be similar to that of U.O.P. catalyst. Considerable differences were observed in the change in octane number by hydrogenation of polymer gasoline:

	High pressure polymer gasoline decreased, 81	→	77 O.N.
Medium	" " " "	more, 81	→ 62 O.N.
High	" " " "	over magnesium phosphate	(hydrog?) 79 O.N.

High pressure polymer gasoline over U.O.P. catalyst (hydrog?) 72 O.N.

p. 179-181 Comparison of the steel and utility requirements for butane dehydrogenation by chlorination and catalytic dehydrogenation. 1942

p. 182-184 Design data for a proposed commercial propane dehydrogenation plant based on pilot plant experience. Capacity: 23,000 tons/year of propylene in 30% concentration. Includes schematic flowsheet giving material balance and operating conditions. Temperature 600°C (inlet to reactor). Conversion 28.3%. May 18, 1943

p. 185 Flowsheet for a butane dehydrogenation plant using several reactor chambers and interstage heaters.

p. 186-191 Isomerization of n-butane over AlCl<sub>3</sub> and supported AlCl<sub>3</sub> catalysts. I.G., Oppau, January 1944. It was found that deactivated AlCl<sub>3</sub>/(on) Al<sub>2</sub>O<sub>3</sub> could be regenerated with HCl. Part of the AlCl<sub>3</sub> appears to form a compound with alumina which is inactive. This compound can be broken up with HCl and thus the freed AlCl<sub>3</sub> is available as an active catalyst. A carrier consisting of bleaching clay with 1% Al<sub>2</sub>O<sub>3</sub> sol. did not form inactive compounds with sublimed AlCl<sub>3</sub> and therefore retained its activity much longer.

p. 192-227 Alkylation of butene-1 and isobutane with sulfuric acid catalyst, I.G., Oppau, November, 1943 and January, 1942.  
 Experimental work in a 3 B/D continuous experimental plant at 32°F with 5 gal. of acid in the reactor and a space velocity of 0.43 volumes of olefins per hour per volume of acid in the reactor. Acid lives of 30-45 were obtained. The higher ones were reached by adding 0.02 % of a sulfuric acid-stable emulsifying agent.

p. 228-231 Fischer-Tropsch in Liquid Phase, ca. 1942.

Description of an experimental plant for which a construction permit was requested.

- (a) Catalyst: fused Fe catalyst similar to ammonia synthesis catalyst.
- (b) Plant capacity 5,000 tons/year of which 2,050 is gasoline; 1,000 is motor oil, 1,100 hard waxes, 250 is alcohol, 250 polymer gasoline, and 350 propylene.
- (c) General description of costs, building materials, power requirements, labor, etc.

p. 232-281 Fischer-Tropsch, Use of Iron Catalyst. September, 1943.

Experimental data from 4.8 l. capacity reactor. Gas analyses, yields, product analyses, and operating conditions are given. Various iron catalysts. No detailed catalyst descriptions. (See pages 329-333 for summary).

p. 282-287 Catalysts for wax synthesis. March, 1943

General discussion on problems of using iron as substitute for cobalt in synthesis catalysts. Description of preparation and properties of Fe/Cu/MgO/diatomite precipitated catalyst. At a space velocity of 120, at 230°C operating temperature, a yield of 150 g./m<sup>3</sup> was obtained with an 84% conversion of CO. The product contained 41% hard waxes. The wax is equivalent to that obtained with cobalt catalyst, containing no olefins and 92-95% straight chain compounds. The initial space velocity was 0.45 kg./liter of catalyst space/day. After several weeks the catalyst activity declined slowly, but the yield of wax decreased more rapidly.

p. 288-291 Alcohol Synthesis from CO and H<sub>2</sub> by the oil recycle process. May, 1940

Alcohols of especial interest were C<sub>12</sub> to C<sub>18</sub>. Gives results of experiments at 20 to 180 atm. pressure with catalyst 997 (Dr. Linckh), with feeds of 3H<sub>2</sub>:1CO and 1H<sub>2</sub>:1CO. Best results were obtained with 1H<sub>2</sub>:1CO feed at 180 atm. Total yield = 170 g./m<sup>3</sup>,

with 9 g. C<sub>12</sub>-C<sub>18</sub> alcohols/m<sup>3</sup> CO + H<sub>2</sub>. No catalyst description. The alcohol yield increased with increasing pressure up to 150 atmospheres. A high hydrogen concentration favors the formation of lower molecular weight products.

p. 292-3

CO + H<sub>2</sub> Synthesis of Wax by oil recycle process. Costs estimate. May 2, 1941

p. 294-295

Summary of the composition of primary products from middle-pressure synthesis. May 6, 1941

A comparison is made between the precipitated Fe/Cu/Al<sub>2</sub>O<sub>3</sub>/K and the cobalt catalysts. For wax production the maximum estimated yields obtainable from the iron catalysts equal the minimum estimated yields from cobalt catalysts.

p. 296

Iron catalysts.

February, 1943.

Summary of status of development of iron catalysts as replacement for cobalt.

Ruhrchemie has developed an iron catalyst on laboratory scale containing Cu and Ca on diatomite operating at 215-225°C at medium pressures. Products contained more olefins and oxygen compounds than with cobalt.

Brabag performed laboratory experiments with iron catalyst at 15 atmospheres and 200-280°C using gas with CO:H<sub>2</sub> ratio of 1.6:1. Yields were the same as with cobalt.

Lurgi: Best iron catalyst required 220°C and 20 atmospheres for a 50-60% wax yield. A reduction in pressure to 10 atmospheres required a temperature rise to 245°C.

Rheinpreussen: Covers experiments on pilot plant scale with iron and iron-copper catalyst, CO:H<sub>2</sub> = 1.6:1. Yields 205-230°C, 150-170 g./m<sup>3</sup>, 35 g./m<sup>3</sup> wax, 37.5 atm. on cooling side; 220-245°C, 175-185 g./m<sup>3</sup>, 50-55 g./m<sup>3</sup> wax 36 atm. on cooling side; total olefins 65% and as high as 80%.

(This summary is identical with that on p. 163 of Bag 2169, Roll 27).

p. 297-301

Iron catalysts as replacement for cobalt. ca. February, 1943.

Short outline given of preparation of iron catalysts, synthesis conditions, yields and expected catalyst life.

p. 302-307

Similar to letter given in pages 297-301. March 1, 1943.



p. 308-309 Iron catalysts.

April 17, 1943

Preparation using halogen containing compounds, especially  $\text{CaF}_2$ , in place of diatomite. Catalyst gave same yields as standard Fe catalysts, but at lower operating temperature. With reduced alkali, the yield of high boiling hydrocarbons decreased while the yield of alcohols increased considerably.

	Standard Catalyst precipitated iron cat. containing MgO on diatomite	Std. Cat. with reduced $\text{CaF}_2$ alkali	Std. cat. with $\text{CaF}_2$ in place of diatomite
Catalyst No.	1298	1459	1389
Temperature	230	230	220
Vapor hourly space velocity	720	720	720
CO conversion	20	24	35
Material boiling below 195°C	10	36	47
" " between 195-250°	6	16	22
" " " 250-320°	10	15	16
" " " 320-450°	18	18	9
" " above 450°	56	13	3
	<u>100</u>	<u>98</u>	<u>96</u>
250-320° Fraction			
% olefins	46	30	23
% alcohols	25	51	39
320-450° Fraction			
% olefins	36	27	19
% alcohols	18	36	16

p. 310-316 Iron catalysts.

May 5, 1943.

Summary of progress. Contains little information except the statement that no iron catalyst has been found to operate at atmospheric pressure.

p. 317-321 Iron catalysts.

May 17, 1943

Summary of the work of different investigators. The yields obtained with vapor and liquid phase operations are given. Though no detailed catalyst compositions are given this report contains

interesting information on:

- (a) Yields with two new catalysts developed by Ruhrchemie, one of which produces a white wax (32% of the hydrocarbon product) while the other permits operation at 200-215°C.
- (b) Yields with sintered iron catalyst in the vapor phase.
- (c) Yields in liquid phase with sludged colloidal catalyst ground with oil.

p. 322-323 Iron catalysts.

May 17, 1943.

Discussion of the progress in the attempts to find a substitute for cobalt catalysts which will involve the least changes in equipment. (The question in all of these discussions seems to be not which is the best catalyst but how nearly can iron catalysts be made to resemble the cobalt catalysts).

p. 324-325

Progress report of new reactors. No details on construction.

December, 1943.

p. 326-328

Brief summary of work on iron catalysts.

November, 1943.

p. 329-333

Iron catalyst

November 8, 1943.

Apparently a summary of the experimental data shown on pages 232-281 of this roll. This report covers the reasons for the experimental work, description of the reactors, techniques for working up experimental data and a summary of the results obtained up to the time of the report.

p. 335-340

Syntheses with CO.

November 8, 1942.

(a) A short discussion on the status of the fatty acid synthesis (laboratory) with CO from olefins. The reaction was carried out at 285-290°C, 200-250 atmospheres, with Ni(CO)<sub>4</sub> as catalyst. Continuous and static experiments are discussed and some yield data are presented.

(b) Acetic acid apparently from methanol and CO. The catalysts are NiI<sub>2</sub> and NiBr<sub>2</sub> in the presence of Cu, Sb, Vd, W, or Mo. Pressure is 280-300 atmospheres, and the temperature 295-300°C. Both acetic acid and the methyl ester are formed.

(c) Adipic acid from tetrahydrofuran. Yields were poor with the same type of catalyst because considerable amount of valeric acid is formed.

(d) Oxo reaction of tetrahydrofuran (with CO and H<sub>2</sub>) etc.

p. 341-349 Production of synthetic lubricating oils by the cracking of hard waxes in the vapor phase at atmospheric pressure and polymerization of the resulting olefins with  $AlCl_3$ . Analyses, properties and yields are tabulated. September 8, 1941

p. 350-353 Patent Application: Production of high molecular weight fatty acids. By treating waxes or high molecular weight alcohols with alkalis in water at high temperatures (230-400°C) and high pressures. June 10, 1944.

p. 355-373 Production of succinic acid from tetrahydrofuran and  $NaNO_3$ . October 2, 1942.

p. 374-423 Testing and evaluations of starting materials for paraffinic lubricating oils. October, 1942.

Waxes available for oil production in Germany (see pages 341-349) were examined for suitability. A vacuum distillation combined with aniline point and density of fractions was used. Much detailed data.

p. 424-466 Observations on Heat Relationships in Hydrocarbon Syntheses after F. Fischer. (A theoretical discussion). March, 1940.

I. Flow in catalyst filled tubes.

II. Heat conductivity in the Fischer Synthesis Catalyst Tubes.

III. Fischer Synthesis from the Standpoint of Heat Theory.

p. 467-480 Iron Catalysts. May 15, 1942

A fairly comprehensive report with much data, giving effect of operating variables (feed composition, reaction temperature, space velocity) on product distribution and yields of olefins, alcohols, and straight chain compounds. Catalyst,  $Fe/Cu/MgO/K$ /diatomite.

p. 482-564 Synthesis of fatty acid esters and fatty acids by reaction of CO with olefins and alcohol in the presence of water. Covers work to December, 1941.

This is a comprehensive report covering the development of a large variety of catalysts on carriers, including copper halides. Conversions up to 95% were obtained and it was found that free acids could be made as easily as esters. It was found that the reaction could be carried out without halogen in the catalyst in the presence of carbonyl forming metals. Metals of fifth and eighth groups were also active. It was definitely established that  $Ni(CO)_4$  is the real catalyst, which gives excellent results in the presence of metal surfaces such as copper.

p. 565-576

A short review of water gas synthesis with iron catalyst up to 1939, and experimental work using gas recycle for heat removal. (One page missing). April 18, 1939.

Attempts to have the catalyst finely divided were given up and a sintered iron catalyst substituted which was able to prevent harmful soot formation. The manufacturing method is outlined. A small amount of potassium was added to inhibit the formation of lower boiling hydrocarbons.

In order to remove the heat of reaction a rapid circulation of the reaction mixture through an outside cooler was tried. A gas recycle ratio of 100:1 was used and permitted a temperature rise of only 10°C in the bed. A small amount of the recycle gas was cooled to a lower temperature than the bulk of the gas in order to remove high boiling products, thus reducing their concentration in the recycle stream and preventing excessive deposition on the catalyst. Operating conditions were 300-350°C and 20 atmospheres. Experiments were on pilot plant scale.

Overall yield was 160 g./m<sup>3</sup>. Products were 80% olefinic with the gasoline containing 3-4% oxygen. After removal of oxygen compounds and subsequent treating as well as polymerization of the gases the following yields were obtained:

Gasoline	78 g.	84-86 research O.N.
Polymer gas	29 g.	97 " "
Diesel oil	23 g.	50-53 cetane number
Alcohols	14 g.	
Wax	1 g.	
	<u>145 g.</u>	

p. 577-580 Patent Application.

Conversion of carbon monoxide with hydrogen. Use of alkali fluoride in catalyst containing iron, copper, and possible heavy metal oxides. 1943

p. 581-586 Patent Application.

Production of Acetylene by incomplete combustion of hydrocarbons with oxygen in a flame reaction after mixing of the gases where the largest extension of the essentially empty combustion space is at right angles to the direction of flow. 1940

p. 587-591 Patent Application.

Removal of fogs, dust and soot from gases. Use of filtration through a packed space containing small pieces of coke or other materials. 1942

p. 592-595 Patent Application.

Production of water gas from hydrocarbons. Use of vapor phase catalyst, such as iron carbonyl, besides the solid catalyst. This is to prevent reactor plugging and inhibit methane formation.

1940

p. 596-602 Patent Application.

Reaction between CO and H<sub>2</sub> with Sintered Iron Catalyst. Addition of metals such as Ag and Cu to facilitate reduction.

1944

p. 603-606 Patent Application.

Production of Liquid Hydrocarbons. Use of CaF<sub>2</sub> as promoter or carrier in Fe/Cu/K catalyst.

1943

p. 607-612 Patent Application.

Production of Acetaldehyde. Reaction of CO + H<sub>2</sub> with CH<sub>3</sub>OH or (CH<sub>3</sub>)<sub>2</sub>O at temperatures below 200°C and at high pressures in the presence of carbonyl forming metals or their compounds.

1941

p. 613-615 Patent Application.

Preparation of olefins from saturates and oxygen in which flame formation or local overheating is avoided by high velocities or vacuum.

1935

p. 616-619 Patent Application.

Preparation of acetylene from hydrocarbons in an electric arc, in which the gases are introduced tangential and not through hollow electrodes and where the ratio of voltage to current in the arc is below 10, preferably below 5.

1941

p. 620-624 Patent Application.

Continuous gas generator using coal, in which the lower portion consists of a screen above which a water-cooled mixer is rotating in a layer of slag.

1941

p. 625-628 Patent Application.

Preparation of H<sub>2</sub>-CO mixtures from hydrocarbons by incomplete combustion with oxygen where the entering gases are largely saturated with vapors of metals of the iron group.

1940

p. 629-637 Patent Application.

Design of low pressure gas burner where the mushroom type burner is placed below the vessel to be heated in an enclosed narrow combustion space in such a way that the flame movement sucks air and gas through the burner and that the flames cover the vessel uniformly and tangentially. 1940

p. 638-640 Absorption of Chlorine in S<sub>2</sub>Cl<sub>2</sub>.

Discussion of difficulties with a commercial absorption column. 1943

p. 641-643 Graphite Oxide.

Discussion of the use of partially oxidized carbon (about C<sub>2</sub>O) as an additive to Diesel oils, where it reduces the delay in combustion, acts as an oxygen carrier, and burns completely. It is hoped that a shortening of the flame and therefore a reduction of the combustion space can be achieved. 1943

p. 644-657 Peroptan (A Triptane-like product).

Process for the preparation of high octane fuel from isobutane and propyl chloride. From laboratory experiments a product boiling between 80 and 130°C was obtained in 90% of theoretical yield. This product resembled isooctane more than it did triptane. Motor octane number was 98. Condensation was carried out at atmospheric pressure and residual chlorides were removed by hydrogenation. Catalyst is aluminum chloride whose isomerization action is also important in this process. Conditions for the reaction are not given. 1944

p. 658-668 Starting coal (to facilitate starting of Diesel truck motors at low temperature).

General discussion of the use, by army Diesel trucks, of a starting aid in the form of tablets consisting of 20% coal extract, 20% Lignin, 30% ammonium nitrate, and 30% nitrocellulose. The tablets are ignited with matches and burn, without appreciable residue, very slowly. The slow heat release was apparently the important feature. 1943

p. 669-676 Diesel fuel additives.

Various ethers were tested for aids in starting cold Diesel engines. General discussion of the problem. 1942

p. 677 Tanol (isooctane).

Description of the Tanol plant at Heydebreck where the starting material is isobutyl oil from Fischer-Tropsch. Isooctane is made from isobutyl alcohol, one of several components of isobutyl oil which are purified and further processed. A simplified flowsheet is included as well as a flowsheet giving throughputs and yields. July 11, 1941