FILM STUDY GROUP

SUBJECT INDEX AND REPORT

T.O.M. REEL NO. 45

Prepared by

STANDARD OIL COMPANY (INDIANA)

Standard Oil Company
(Indiana)

TECHNICAL OIL MISSION

MICROFILM REEL 45

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Microfilm Reel 45
(Original Identification Reel 13B)

TECHNICAL OIL MISSION
U. S. BUREAU OF MINES

Screened by Standard Oil Co. (Indiana)

Bag 3441
Target 30/5.01
Ruhrchemie, Sterkrade-Holten
~~ITEM 73. SOAPS FROM FATTY ACIDS WASHED OUT FROM PRIMARY PRODUCTS~~

Frame 1, Fatty acids from waste liquors of the synthesis plants in the Ruhr region. October 19, 1942

An estimate is given of the probable amount of fatty acids which could be obtained by the alkali treatment of synthesis wastes. Around 9 tons per month are available which might be used for the manufacture of soap. In order to obtain the maximum amount it was proposed that all licensees and processors should be required to exchange information and experience.

Frame 2-8, Direct production of fatty acids from large scale units, (manuscript) January 24, 1942

The points covered include: A. Raw materials, B. Possibility of recovery, C. Purified fatty acids, D. Fractionated vacuum stilling of fatty acids and E. Results. Frame 9 is a diagram of a fatty acid plant.

Frame 10, Manufacture of soaps. May 26, 1942

About 100 liters of caustic-washed produce were partially neutralized with H_2SO_4. The fatty acids obtained have a very unpleasant odor. About 70% boil below 265°. The acids boiling above 265° were purified and saponified, and produced a soap with good lathering qualities. It was not suitable for use as a toilet soap on account of the odor, but it might be used for laundering and general cleaning.

Frame 11, Production of soap from the alkali treatment of condensate wash in Fischer synthesis. April 21, 1942

The wash liquors are passed through a filter containing spent activated charcoal and into an agitator. In the agitator, which has only a slowly running stirrer, the charge is intermittently saturated with sulfuric acid. A fatty acid layer then forms on the sulfate liquor. The agitator lid has an overflow which leads to a tall saturation vat provided with stirring mechanism. By forcing water under pressure into the sulfuric acid saturator, the level is raised until the fatty acids overflow and pass into the soda-saturation vat. Water is added until all the fatty acids are displaced. The sulfate liquor is then withdrawn from the bottom. The fatty acids in the soda saturator are treated with soda ash and stirred. Here foaming occurs, therefore it is desirable to adjust the stirrer so that it beats the froth well. The consistency of the fatty acids increases after the addition of sufficient soda until saturation is reached. The resulting soap melts from heat of reaction and differs from its original state. It hardens upon cooling.

Frames 12-14 are practically illegible handwritten pages. Frame 15 comprises a flowsheet: Manufacture of soaps from primary fatty acids.

ITEM 74

Frame 16-25, Proposed patent application, dated July 7, 1943, Process for recovery of carboxylic acids or derivatives from alkaline wash liquor concentrates

These frames either contain two applications or two copies of the same one. It is difficult to determine.

ITEM 75. LEAD SENSITIVITY OF VARIOUS GASOLINES

Frame 26-27, Lead sensitivity

A table of values, undated.

Frame 28

Octane number of mixtures of varying amounts of lead with a mixture of:

66% RCH "Grundbenzin"
34% motor benzol

Frame 29-30

Curves show the lead sensitivity vs. octane number as determined by Research method and Motor method.

ITEM 76. USE OF TAR OIL IN GAS TURBINES FOR THE AIR FORCE

Frame 31-32, Tar Oil and the utilization of tar oil and crude oil in gas turbines for the Air Forces. October 11, 1944

In the operation of a gas turbine, the fuel is burned in a combustion chamber into which it has been sprayed through a nozzle, the resulting gases are utilized to operate the gas turbine. Two fuels were tested, one boiling 100-300°C, produced in synthesis or hydrogenation plants, the other a crude petroleum. Both fuels required preliminary purification. The principal fault lay in that the flowpoints were unsatisfactory, since they were too high to meet the requirements of the Air Force.

Frame 33-36, Utilization of tar oils in military aviation. October 5, 1944

The use of tar oils as fuel for gas turbines resulted in serious coking of the spray nozzles when the oils were mixed with air and supplied at temperatures of around 400°. Frame 34 gives a table of the proportions of individual hydrocarbons in the primary products of normal pressure and medium pressure synthesis.

Frame 37-38, Tests with tar oils

A letter states that oil with end point of 320°C is available in quantities amounting to 60,000 to 70,000 tons a year. Lowering the end point would result in decreasing the amount by about 50%.

Coking of the nozzles may be avoided by redesigning so that the hot oil comes in contact with air for combustion only after it has left the jet. Overheating of tar oil must be avoided. A redistillation might remove undesirable tarry constituents.

Frame 39-42 comprise manuscript notes and tables giving the properties of various crudes and tars.

ITEM 77. PROPYL ALDEHYDE, REPORTS

Frame 43-56, Program and reports on synthesis of propionaldehyde, March 1942.

Various catalysts were used, many of which contained cobalt. Using ethylene and water gas as reaction mixture.

ITEM 78. OXO SYNTHESIS

Frame 57-60, Method of fatty acid synthesis at Holten, Leuna and Ludwigshafen

A general conference on the above subject brought out the following:At Holten the process operates discontinuously. The olefin-catalyst slurry is pumped into the vertical Oxo unit cold, and at normal pressure. After compressing with water gas and heating, the gas in the circulation system is passed through the catalyst suspension until no more gas is absorbed. The reaction time is from 30 to 60 minutes. The Oxo product is then transferred to the preheated hydrogenation unit under H_2 pressure and hydrogenation is effected by introducing hydrogen into the circulation. This operation too requires 30 to 60 minutes. After the product is filtered, the catalyst on the filter is slurried with fresh olefin and again introduced to the Oxo unit in which pressure has meantime been released.

At Leuna a continuous process is used. The catalyst-olefin suspension is pumped out of the slurry tank into the top of the Oxo unit which is kept under pressure. The desulfurized water gas is preheated and forced through the suspension from the bottom upwards. The residual gas, leaving the unit at the top, contains volatile cobalt compounds which are scrubbed out by treatment with fresh olefin under pressure. The suspension is then passed to the hydrogenation unit.

At Ludwigshafen the following method is used: The Oxo furnace is continuously charged with preheated feed-oil which contains the cobalt fatty acid salt in solution. Water gas, likewise preheated, passes from the top downard through the unit, and after leaving the converter gives up its heat, through a heat exchanger, to the fresh gas. The Oxo product is conveyed into a decobaltizing column which operates so that the aldehyde product trickles down from the top through a column filled with pumice, while a stream of hydrogen is directed against it. When the cobalt solution again reaches the feed stock, the cobalt-free, almost colorless aldehyde is forced by pressure into the hydrogenation unit, where hydrogenation is achieved in concurrent operation.

A program for further study included preparation of cobalt carbonyl, Oxo-reaction with carbonyls, decobaltizing and cobalt regeneration, and hydrogenation with a Cu-Cr-O catalyst. Frame 60 is a diagram of an Oxo plant.

Frame 61, Experiments on Oxo synthesis.
November 17, 1941

It is proposed that experiments be made to determine the effect of Co in the aldehyde-catalyst mixture. Parallel experiments should use water gas in one instance and pure hydrogen in the other. In the hydrogen reaction, Cu-Cr oxide catalysts would be used.

Frame 62

It is proposed, in a letter, dated Nov. 13, 1941, that catalyst mixtures suitable for use in the Oxo synthesis should be brought into a lump form.

Frames 63-64 are manuscript pages from an unidentified notebook, and are illegible.

Frame 65-67, The Oxo synthesis,
January 22, 1942

In a continuous process for Oxo synthesis, two possible methods of operation are: pumping the gas through a column of liquid, and causing the liquid to trickle through a packed column. Each method has some disadvantages. It is proposed to construct the liquid column in such a way that it is divided into sections which make possible an increase in concentration. A drawing represents several possible arrangements of such sectioning.

Frame 68-71, Program for Oxo synthesis, particularly for production of propionaldehyde. Nov. 27, 1941

The program includes: A. Separation of C_3-aldehyde, using a high-pressure circulating pump; B. Solid catalysts, with study to learn whether carbonyl formation can be avoided by operating at a lower CO-partial pressure; regeneration by dry treatment with hydrogen at 300-400°C, regeneration by treatment with concentrated water gas under conditions favorable to carbonyl formation; use of wet-reduced cobalt and of cobalt precipitated according to the usual procedure. C. Carbonyls as catalysts. It is noted that all metal carbonyls are poisonous, therefore the operators must take safety precautions. D. Colloidal cobalt as catalyst.

Frame 72, August 5, 1943

"We have already attempted to react water gas with chlorine-containing olefins, but without success. These experiments were made using a slurried cobalt catalyst. The cobalt always removed the chlorine.

"I now ask permission to see whether the chlorine remains unchanged in the olefin if the cobalt or iron is used in the form of a dissolved carbonyl."

ITEM 79. PRODUCTION OF ALCOHOL

Frame 73-74, Alcohol production in circulation synthesis. December 14, 1943

The conditions are noted for a proposed operation to be started about the middle of 1944. This is in connection with a recycle synthesis, using cobalt catalyst.

Purified water gas is conducted to the synthesis furnace. Residual gases are combined and passed to a separator, where they are subjected to cooling in six condensers connected in parallel. Condensate oil is removed and residual gases are passed over activated carbon.

By treatment with caustic, alcohols are obtained. With a throughput of 75,000 cu. meters/hr. of water gas, a yield of about 90 g. liquid product/cu. meter water gas is obtained. From this about 1.6 tons per day of alcohol could be recovered.

Frame 75-79, Recovery of alcohols from the waste waters of synthesis. Nov. 4, 1943

A mixture of alcohols, aldehydes and ketones is present in the pressure condensate from pressure synthesis. A study was made of methods for determining and recovering the alcohols from this condensate. The alcohol content varied from 0.5 to 1.5%, depending on the source of the condensate.

Fairly large samples were distilled and the first distillation was effected under alkaline conditions. After about 10% of the material had passed over into an ordinaryretort, it became evident that all of the alcohols had been distilled. This distillate was then redistilled under a reflux column. Thereby the alcohol content was increased up to 30-40%.

After the lower-boiling alcohols are removed, it is desirable to attach a new receiver since the higher boiling alcohols are only slightly water-soluble and a gravity separation occurs. No definite statements are made so to the precise nature of the alcohols obtained.

Frame 80-84, Alcohol recovery from waste
liquors of the active carbon
(A.-K.) plant. by Dr. Sohne

Experiments were made to determine the advisability of recovering the alcohols (including a mixture of alcohols, aldehydes and ketones) from the non-acidic, oxygen-containing products from the Fischer process. Since the concentration of such substances in the waste liquors was low, averaging 0.4% , it was necessary to study the economics of the proposal. Alcohols from C_1 to C_5 were identified.

Quantitative study and identification were extremely difficult and complete removal of water was impossible by the use of distillation alone. Samples were sent to various laboratories for evaluation, but the reports of results were not in agreement.

Frame 85-87, Results of study of sample sent
to Reichmonopolverwaltung fur
Branntwein. November 24, 1942

The waste liquor contained about 0.4% alcohol; the alcohol mixture had approximately the following composition:

methanol	10%
ethanol	15%
propanol	20%
butanol	40%

The residue consists of higher alcohols.

Frame 88-89

Report of conference on the direct recovery of higher alcohols from CO and hydrogen. June 8, 1943

ITEM 80. ISO SYNTHESIS

Frame 90-95, Iso synthesis.
June 17, 1943

In a discussion on Iso-synthesis, the proposed experimental conditions are noted. In order to prevent coking up of the reactor tubes, a copper lining was suggested. The path of the gases along the catalyst should be so regulated that a minimum of carbon deposition occurs.

A table gives the analysis of residual gas from reactions using ThO_2, ThO_2ZnO, and $ThO_2 = Al_2O_3$, at 300 atmospheres pressure and 450°C temperature.

ITEM 81. IRON CATALYST FOR OLEFIN PRODUCTION

Frame 96-97

Iron catalyst. (2 pages of manuscript)

Frame 98-99, Olefin hydrocarbons,
September 4, 1941

From carbon monoxide and steam, liquid products were obtained which were apparently completely olefinic. The catalyst contained about 50% nickel in addition to iron. The residual gas contained appreciable amounts of H_2, ranging from 6 to 10%.

The suggestion is made that the high olefin content may be caused by shifting the CO/H_2 ratio in the direction of the CO end. The question is raised as to the dependence of the degree of saturation upon the concentration of CO and H_2.

Tests are proposed with the following gas mixtures:

synthesis gas -	$CO:H_2 = 1:2$
water gas	$CO:H_2 = 1:1$
CO-rich gas I	$CO:H_2 = 2:1$
CO-rich gas II	$CO:H_2 = 4:1$

It is hoped that from the values obtained in these tests, optimum relationships can be developed which may lead to full olefin production

ITEM 82. RECOVERY OF FATTY ACIDS FROM WASTE NEUTRALIZATION LIQUORS
BY DR. OHME

Frame 100-106, Recovery of fatty acids

It is recognized that in medium pressure synthesis, certain amounts of fatty acids are formed, along with the hydrocarbons. These fatty acids are contained, in vapor form, in the residual gases which leave the furnace.

During the condensation of the products and the water of reaction, which condensation in medium pressure synthesis is always accomplished by indirect cooling, the fatty acids might give rise to serious corrosion in the condenser and the parts of the unit which are connected to it. For this reason, it is absolutely essential that the small amounts of fatty acids shall be neutralized in the vapor phase before they are condensed. This is accomplished by spraying the residual gas with a soda solution, whereby the fatty acids contained in the gases settle out in the form of their sodium salts in the spent caustic. For reasons of operating conditions, and especially in order to avoid unnecessary loss of alkali, it is customary to proceed with very dilute soda solutions. Operation with concentrated solution and repeated injection - that is a caustic circulation - cannot be considered since difficulties due to emulsion formation arise when the oil is separated from the caustic. In medium pressure synthesis, therefore, it is unavoidable that the waste liquors from neutralization shall present a highly dilute soda solution which contains in the solution fatty acid sodium salts, with extremely low percentage of fatty acids. The concentration of unused alkali in the waste liquor amounts to around 0.5% and the concentration of fatty acid to about 0.5-1.0%. These very dilute soap solutions have not, heretofore, been subjected to further treatment at any plants, since it seemed that the recovery of these fatty acids could not be accomplished economically even if it could be done successfully.

Although the residual gases are neutralized with soda solution, there are always certain amounts of fatty acids to be found in the condensates. These residual fatty acids proceed, in part, into the water of reaction and in part into the oil condensate, and at present are probably generally removed from the condensate oil by caustic washing. The amounts of fatty acids thus recovered with the aid of caustic wash are probably all supplied for some sort of use at present. These amounts are however only scant in proportion to the amounts of fatty acids which are lost in the neutralization liquors.

Aroused by the war-caused scarcity of fatty acids, experiments were started on recovering from the waste caustic the fatty acids which it contained. By intensive examination of relationships, we found a usable method which enables us to recover the fatty acids in about 90% yield, in an economical fashion. The studies, first carried out in the laboratory, led in the summer of last year to the erection of a commercial unit, which has been in continuous operation since September and has fulfilled all expectations. Before I enter into a more detailed explanation of this process, I should like to touch upon a few other possibilities which might also eventually be applied to the recovery of the fatty acids contained in the waste liquors. I must state first, however, that these attempts have not produced any successful results, since the methods in question afford the recovery of only a small fraction of the fatty acids which are present. In connection with this problem, we examined the possibility of precipitating the fatty acids from dilute solutions using lime. We must however admit that the solubility of the lime salts of the fatty acids is too great, or their concentration is too small, to obtain a practically quantitative separation.

Even with repeated precipitation of the sodium salts of the fatty acids by means of lime separation, was not achieved. For example, using a caustic lye which contained about 10 g. fatty acid per liter, we obtained through twice precipitating with sufficient excess of lime about 2.3 g. of fatty acid, that is, only about 25%. To be sure, it was shown, on investigating the fatty acids thus recovered, that only high-boiling fatty acids had primarily been precipitated. Of these, 72.2% were from C_8 upward. An economic recovery by this method was not therefore to be considered.

We attempted further to release fatty acids by passing carbonic acid through acidified dilute solution. When the current of CO_2 passed through the acid solution at a temperature of 95 C, we were able to recover 3.6g/liter $\cong$ 36% from the initial liquor, which again contained about 10g/liter. Here too, the yield, that is the possibility of recovery, was too scant to afford an economic application, expecially since, in both lime precipitation and in CO_2 treatment, considerable amounts of acid were required to neutralize the lime or to acidify the solution.

I now come to a discussion of the actual method as we applied it. We first examined the possibility of recovering the fatty acids by extraction with suitable solvents, after the fatty acids had been freed from the liquors by acidification with hydrochloric or sulfuric acid. A general requirement of the solvent is that it shall have practically no solubility in water, in order that the losses through waste liquids may be kept within tolerable limits, since considerable amounts of water are always present in the extraction process. As a suitable extraction agent, for example, we could use trichloroethylene, or perhaps the light naphtha which had been produced in the synthesis itself. By suitable choice of operating conditions in the extraction, it is possible to accumulate practically the total fatty acid content in the solvent. The solvent containing the fatty acids can then be worked up in various ways. The fatty acids can be recovered by distillation, in which case the solvent must meet the condition that its end boiling point shall lie below the initial boiling point of the lowest fatty acid to be recovered. A second method consists in releasing the fatty acids from this extraction agent which contains them by means of a wash with caustic soda. The soda wash can be enriched with fatty acids so far as practicable, and the fatty acids later freed by treatment with mineral acid. The second method appears at first glance to be more complicated. Nevertheless we decided upon this process for various reasons. The advantages of recovering the fatty acids from the solvent by means of caustic wash lie in the fact that at least in those portions of the apparatus which come in contact with the solvents, no corrosive attacks are to be expected due to the fatty acids, since the solvent is almost continuously freed of fatty acids by alkali. A distillation process from the extraction agent would make special requirements of corrosion resistance upon the distillation apparatus. Moreover it is necessary to place special stress on an exact end boiling point of the solvent, which is as low as possible, since the lowest boiling fatty acids always have a low boiling point, for instance acetic acid boils at 118°C. A further disadvantage in separation by distillation is that certain residual amounts of oil remain in the solvent extract and produce a definite amount of unsaponifiable material which remains in the distilled fatty acids. This undesirable condition is likewise avoided when the fatty acids are neutralized out of the solvent by caustic wash.

In consideration of the above findings, we constructed the plant which is currently operating, about as follows:

The residual liquors from the I., II., and III. stage are acidified, with the aid of a simple proportioning device, using sulfuric or hydrochloric acid to obtain a definite pH value - about 5 - 6.5 - and then extracted in continuous operation with the light naphtha which resulted from the synthesis itself. This light naphtha is always circulated in a closed cycle. To achieve a sufficient removal of water, only an extremely simple piece of apparatus is required, consisting essentially of a mixing tube and a separator. The extraction naphtha, forced by pressure through the extraction apparatus, is then propelled immediately after the extraction through a caustic soda wash, such as is customary in scrubbing normal naphtha, thus only one pump is required for circulating the naphtha.

The caustic soda is likewise circulated, and is changed after it is sufficiently enriched with soaps. After the soap-enriched caustic is exchanged, it is decomposed with sulfuric acid, and the fatty acids, which are not present in concentrated condition, separate in a sharply defined layer. Emulsification of the naphtha with the soap solution, which might be anticipated, can be readily controlled.

As an interesting phenomenon in the extraction of waste water with naphtha, it may be mentioned that it is possible, by suitable choice of proportions between liquor and naphtha, to influence within certain limits the composition of the fatty acids obtained. With a high excess of naphtha over residual liquor, it is possible to extract completely the lower fatty acids such as acetic and propionic, while with slight naphtha excess these water-soluble fatty acids can only be extracted to a partial extent. Since the lower fatty acids are practically equally soluble in water and in naphtha these acids are distributed in the naphtha and the liquor according to their partition coefficients. The more naphtha that is used, the more of these lower fatty acids that can be scrubbed out. This fact can be utilized practically if the fatty acids are to be recovered for some particular use. For example if for some reason the proportion of lower fatty acids is to be kept as small as possible, the extraction will then be done with correspondingly small amounts of naphtha. If however it is important to recover all the fatty acids, correspondingly larger amounts of naphtha are used. The fatty acid compositions which we obtained when operating with varying amounts of naphtha are for example the following:

For Case I, to 1 part liquor, 0.5 parts of naphtha were used. It proved that up to and including C_4, only 7.5% were obtained while the rest consisted of higher fatty acids. In Case II, where 1 part of liquor was treated with 4 parts of naphtha, the proportion of acids up to and including C_4 amounted to 29.5%. When intermediate amounts of naphtha were used, the proportions of lower fatty acids lay between the two limits.

By this procedure it is also possible to obtain a separate recovery of particularly high, and predominantly low fatty acids, if the operation is carried out with two separate systems of naphtha circulation; here the naphtha of the first extraction extracts primarily the higher fatty acids.

while in the second circulation the lower fatty acids are recovered. Operating in this manner, with two stages of extraction, or even in one stage with sufficient excess of naphtha, it is possible to recover up to 95% of the fatty acids present.

Considered in the absolute, these amounts of fatty acids are relatively small, since they make up only 0.2-0.3% of the total primary reaction products, so that they have scarcely any importance in the consideration of an entire plant. When, however, one considers the extreme scarcity of fatty acids, and also the fact that the amount of fatty acids to be added to finished products is often relatively slight, it is evident that by recovering even these small amounts of fatty acids, a very considerable increase in the products prepared from them becomes possible.

In conclusion it may be noted that the recovery of these fatty acids, even in these minute amounts, can be accomplished economically since the installation and service costs are so low that they scarcely need to be taken into consideration. Special service personnel is practically unnecessary since the two required pumps can be located in a single pump house. The operating expenses for acid and alkali are also adjusted so that they can be borne, even though it may seem at first glance as though the expenditure of acid and alkali might be too great in view of the large volume of water to be treated. For example, in our case the average operating expense for the plant amounted to 0.15 to 0.17 RM per kilogram of acid. These costs are supportable since the market price of fatty acids from C_{10} up is around 0.74 RM per kilogram. The fraction of C_{10}-C_{20} acids is between 55% and 60% of the total fatty acid.

As has already been mentioned, the plant costs are extremely low, since we used normal iron for the entire installation.

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Note: The rest of this article is too dim to be legible.

ITEM 83. COOLING AND CONDENSATION PLANT

Frame 107, Cooling and condensation installation for synthesis gas. (Diagram and flow sheet)

ITEM 84. LARGE SCALE RESEARCHES, 1935

Frame 108-162, June to August 1935

A collection of data sheets concerning the operations of furnace, operating conditions, charges, etc.

ITEM 85. INFLUENCE OF LENGTH OF CATALYST BED

Frame 163-168, Length of catalyst bed.
October 11, 1935

A letter transmits five sets of curves showing the influence of the length of the catalyst bed upon performance. In normal laboratory operation, no appreciable drop in yield is noted up to 1000 hours. There is no indication of the formation of an inactive zone upon the entry of the gases.

ITEM 86. HYDROGEN REVIVIFICATION

Frame 169-175

A discussion on the subject of catalyst regeneration is summarized as follows: It may be stated that hydrogenation under the given conditions, hydrogenation temperature from 200-225°C, and H_2 throughput of 1000 cu. meters/hr. causes an effective regeneration and increased life for the catalyst which has been damaged by paraffin deposits. Compared with production from units without hydrogenation, over 2000 hours operating time - a production increase of about 0.25% can be attained. However there are a few disadvantages.

Frame 176-177, Hydrogen treatment of the
gasoline catalyst. Nov. 22, 1935

Frame 178-181, Report on hydrogenation and
runs at the Rauxel pilot plant.
Nov. 1, 1935

ITEM 87. TOTAL LIFE OF CATALYST

Frame 182-186, Extension of operating time
by short revivification
Nov. 22, 1935

An appreciable lengthening of catalyst activity was achieved by undertaking regeneration before the catalyst was completely spent, at temperatures of around 200°C. It appears desirable to practice regeneration at short intervals and from the very beginning of the operation.

Frame 187-189, Second conference on Extension
~~of operating time by short~~
revivification. Dec. 3, 1935

Results from laboratory and large scale operating showed that the effects of the new method of regeneration were favorable.

ITEM 88. PROGRESS OF REACTION DOWN THE CATALYST BED

Frame 190-195, Carbon monoxide conversion at
different catalyst depths.
Nov. 25, 1935

The conversion at various depths of catalyst is shown graphically in a series of curves. The data from which the curves were developed were obtained partly from large scale experiments and partly from laboratories at different units.

ITEM 89. RESIDUAL GAS COMPOSITION WHEN SYNTHESIS GAS CONTAINS MUCH CARBON DIOXIDE

Frame 196-197, Feb. 3, 1936

It was found that a residual gas containing 14% CO_2, if it had not been scrubbed, produced about 100 g. average product; of this 10-15% was gas oil and about 2% paraffin. When the CO_2 was removed by scrubbing, a yield of from 118-133 g. was obtained.

Frame 197-198, Feb. 3, 1936

From a synthesis gas having the composition:

CO_2	14.0 %
CO	27.0
H_2	55.3
CH_4	1.0
N_2	2.7 %

after is has passed once over the catalyst, a contraction of 60% occurs.

The composition of the end gas is:

CO_2	35.0%
Saturated HC	2.0
CO	16.0
H_2	33.0
CH_4	7.5
N_2	6.5

When worked up in two stages, the composition after the second stage is:

CO_2	47.0%
Saturates	1.0
CO	8.5
H_2	17.5
CH_4	17.0
N_2	9.0

If the CO_2 is scrubbed out prior to the conversion, the gas, after scrubbing has the composition:

CO_2	0.2%
CO	31.0
H_2	64.4
CH_4	1.2
N_2	3.2

This is subjected to single stage conversion and produces:

CO_2	8.0%
Saturates	3.0
H_2	44.3
CO	21.5
CH_4	14.0
N_2	9.3

When given 2-stage conversion the product (after the final stage) is:

CO_2	5.0%
Saturates	3.0
CO	16.0
H_2	31.5
CH_4	27.5
N_2	16.6

Frame 200-203, Determination of heating value of residual gas, as a makeup gas for synthesis

ITEM 90. FORMATION OF PROPYLENE

Frame 204-205, Propylene, June 10, 1936

It was found that under normal conditions of synthesis gas conversion, approximately 3.0% of the 30% of the "gasol" produced consisted of propylene. However, if the proportion of hydrogen was increased, the formation of unsaturates was suppressed.

ITEM 91. AVOIDING WAX FORMATION

Frame 206, August 19, 1935

In order to avoid the undesired formation of paraffin wax in the low-temperature reactors, it is proposed that the proportion of hydrogen in the synthesis gas be increased until the hydrogen is present in excess.

ITEM 92. NAPHTHALENE IN SYNTHESIS

Frame 207-209, The effect of naphthalene upon the course of the synthesis. Jan. 9, 1937

In a study to determine the effect of naphthalene, a normal catalyst containing 9.0% ThO_2 was used. The catalyst was reduced at 350° with 300 liters of H_2, N_2 for three quarters of an hour, and placed in operation at 180°C with synthesis gas. The temperature was then raised to 185°C. After a 34-hour run, the synthesis gas was passed, before reaching the catalyst, through a naphthalene-filled chamber so that it might become charged with naphthalene.

The naphthalene was found to have an injurious effect on the catalyst; it was carried along unchanged into the endproducts.

ITEM 93. FORMATION OF CARBON DIOXIDE: CORRECTION

Frame 210-212

A correction to information previously given.

ITEM 94. EFFECT OF AMMONIA

Frame 213, Ammonia. Nov. 19,1937

It was stated that the addition of ammonia to the synthesis gas caused deterioration of the catalyst in pressure reactions. It should be ascertained whether or not this was also true in synthesis without pressure.

Frame 214-215, Sept. 2, 1941

Two patent applications from Brabag.

One, B 182020, proposes to increase the activity of the catalyst, by treatment at synthesis temperature with gaseous ammonia. The results of experiments were not favorable, and the statements in the application were considered to be unfounded.

Application B 181,294 proposes increasing the activity and effective life of the catalyst by a cautious oxidizing treatment, prior to contact with the synthesis gas. Results of experiments to test this proposal did not indicate any appreciable advantage or disadvantage.

Frame 216, Ammonia. July 4, 1941

A letter of the above date states that the use of ammonia causes a decrease in yields.

ITEM 95. MECHANISM OF SYNTHESIS

Frame 217-218, Synthesis Feb. 17, 1939

~~Experiments were proposed, to try to learn whether alcohols can~~ be readily reduced to hydrocarbons over a normal cobalt catalyst, at 185°C with normal pressure.

Frame 219, Formate theory. March 22, 1944

Recent experiments have shown that sodium formate, in the presence of an iron catalyst, is decomposed by hydrogen in the temperature range of synthesis gas, with the formation of carbon dixoide. Frames 220-222, dated Dec. 11, 1937 are too faint to read.

Frame 223, Nickel products. May 14, 1943

The formation of oxygen-containing by-products seems to occur only when cobalt or iron catalysts are used. It is suggested that nickel catalyst should be tested, to learn the nature of the primary products of medium pressure synthesis.

Frame 224, Osmium. July 1, 1943

A proposal is made to test osmium as a possible catalyst for the Oxo process.

ITEM 96. SYNTHESIS AT LOW TEMPERATURES

Frame 225, Effect of low temperature.
Dec. 18, 1937

The importance of avoiding temperatures which are too low is stressed. Frame 226 gives a series of curves showing the effect of catalyst preparation at different temperatures.

ITEM 97. RESULTS IN OVENS 23 AND 29

Frames 227-229 contain charts which show in graphs the results obtained from ovens 23 and 29 from November 1937 to January 1938.

ITEM 98. SYNTHESIS FROM DEUTERIUM AND CARBON MONOXIDE

Frame 230, Hydrocarbons from heavy water.
February 5, 1938

The conditions of an experiment with 100 cc of normal water were: electrolysis of the water, and then passage along with CO from formates over the catalyst. The question was raised whether the same conditions should be maintained in a test using heavy water.

Frame 231, Paraffin from heavy water.
October 12, 1938

The heavy water was decomposed by electrolysis, and the hydrogen was mixed with CO from formic acid and passed over a normal Co-Th catalyst at normal pressure; from 90 g. heavy water at 168°C in 400 hours, with a contraction of 63% the following yields were obtained:

19 g. deuterium paraffin
17.5 cc deuterium oil

a yield of about 50%.

ITEM 99.

Frame 232, The effect of introducing an active carbon scrubber between the two stages of the operation

This is a series of curves.

ITEM 100. OLEFINS IN PRODUCT FROM THORIA-MAGNESIA CATALYST

Frame 233-234, Olefin content of naphtha from Th Mg catalysts. May 31, 1938

This is a note on the different results with regard to the olefin content of products, at Rheinpreussen and at Ruhrbenzin.

Frame 235, Suppression of methane formation by adding ammonia March 24, 1938

ITEM 102. THEORETICAL YIELDS

Frame 236, Possible theoretical yields dependent upon the proportion of consumption in gasoline synthesis. July 2, 1938

A series of curves.

ITEM 103. EXPERIMENTS WITH VARIOUS CATALYSTS

Frame 237-241, Manuscript pages from an unidentified notebook

ITEM 104. SYNTHESIS STATUS, 1938-1939

Frame 243-246, Status of normal and pressure syntheses. Jan. 5, 1939

This is a report of a conference between a group of research men. Results which had been obtained at various laboratories are noted. Among the problems considered were: loss through excess CO_2 formation, cause of methane formation, increasing the yield of liquid products, conditions of operation, catalyst manufacture, etc.

Frame 247-253

A notice, dated Sept. 16, 1938 on various problems connected with gasoline synthesis. The first 4 pages are too dim to be legible.

ITEM 105. SEPARATION OF CARBON ON THE CATALYST

Frame 254-255, Carbon Deposition November
<u>19, 1938</u>

Studies with varying ratio of $CO:H_2$ were made to determine, if possible, the cause of excess carbon deposition on the catalyst. It was suggested that the presence of additional CO_2 might lessen such deposition.

ITEM 106. INCORPORATION OF AROMATICS

Frame 256, Aromatics. March 31, 1939

A letter of the above date comments on a proposal to introduce aromatics into the catalyst chamber of the hydrocarbon synthesis unit, with the hope of producing mixed paraffinic-aromatic or naphthenic oils.

Previous experience indicates that pure benzene passes through the process unchanged, while commercial benzol, containing thiophenes, causes a poisoning of the catalyst.

ITEM 107. IRON CATALYST EXPERIMENTS

Frame 257-260, Iron catalyst syntheses
December 12, 1940

Data concerning the synthesis with recycled water gas using an iron catalyst prepared from 100 Fe, 10 Ca, 5 Cu, precipitated with 100 kg KOH:

1	Duration of test	70 days
2	Temperature	243°C
3	Gas pressure	20 atmospheres
4	Circulation	1 + 2.7
5	Addition of $CO + H_2$	76%
6	$CO + H_2$ degree of liquefaction	54.5%
7	Yield	107 g. liquid +14 g. "gasol"
8	Boiling range of liquid products:	

Naphtha	-200°C	37% weight
Oil	200-320 °	16%
Soft wax	320-460	14%
Hard wax above	460	31%

With reference to the various products the following may be noted:

1. Catalyst life is less than that of the cobalt contact.
2. Temperature range lies between 235-260° (30-50 atmospheres steam pressure).

3. Gas pressure must be around 20 atmospheres.

4. The ratio of $CO:H_2$ must be maintained by adding 1 + 3 in makeup in the recycle, otherwise there is excess formation of CO_2 and deficiency in water formation.

5. In the first stage, 70-75% of the $CO + H_2$ present are converted, the rest must be worked up in the second stage.

6. The analytically determined degree of liquefaction is about 3% lower than with cobalt catalyst.

7. In two-stage operation, a total conversion of 140 g. including gasol is obtained. One sheet of curves represents the results.

Frame 261, II-Stage iron synthesis
March 20, 1941

A brief note concerns the study of introducing a treatment of gas between the first and second stages of a two-stage process.

Frame 262, August 19, 1941

A letter concerns a proposed patent application on the preparation of liquid hydrocarbons using iron catalyst.

Frame 263 - a manuscript excerpt from a notebook.

Frame 264 - a work schedule for two weeks.

ITEM 108. COMPARISON BETWEEN IRON AND COBALT CATALYST SYNTHESIS

Frame 265-271, Synthesis by means of iron
catalysts. Jan. 31, 1941

I. Synthesis with iron catalysts

The use of iron as a catalyst for the hydrogenation of carbon monoxide to produce higher hydrocarbons goes back as far as 1913. Later Franz Fischer and his coworkers carried out their final experiments on normal pressure synthesis, also with iron catalysts. However, the results obtained with iron at that time were still very unsatisfactory, particularly in comparison to the cobalt catalysts.

Recently appreciable advances have been achieved by extending to iron catalysts the experiences gained in the interim with cobalt catalyst, especially if it is of definite significance that the synthesis is no longer accomplished at normal but at increased pressures. As the most favorable pressure range was proved to be the range of the so called medium pressure synthesis, namely 10-20 atmospheres.

It has long been known that with iron catalyst, in contrast to cobalt, oxygen is entirely or mainly removed as carbon dixoide. Accordingly the various groups which have heretofore occupied themselves with the development of iron catalyst, have without exception used CO-rich gases which contained more carbon monoxide than normal water gas. Such gases, however, are not technically available without further processing, and are relatively difficult to prepare.

It was therefore a decided advance when we were able, by means of the composition and method of preparation of our novel iron catalysts, to regulate the proportion of carbon monoxide to hydrogen at will, within a certain but rather wide range. In particular we were able to prepare iron catalysts which consume carbon monoxide and hydrogen in exactly the proportion of normal water gas. In this way, the necessity for preparing special synthesis gases containing more carbon monoxide than water gas was eliminated.

Gas production for operating with iron catalysts comprises just the same installations as for cobalt synthesis, namely normal water gas generators and the usual rough and fine purification for the removal of sulfur.

Our catalysts are precipitation catalysts, in whose preparation fundamentally the same operations are used as for previous catalysts. Accordingly a transition from the use of cobalt to iron is possible in the present catalyst factories without notable alteration.

Our iron catalysts contain in addition to iron, certain portions of mineral constituents which can be processed generally and cheaply, as well as more or less large amounts (according to the desired synthesis) of carrier substances such as kieselguhr. The completed contact mass is reduced just like the cobalt catalysts, and in the same apparatus using hydrogen, and can be transported in the usual manner to the synthesis units using air-tight containers. In the reduced condition the grain hardness of iron catalysts is better than that of cobalt catalysts.

With regard to reaction temperature there is a considerable difference from cobalt catalysts, since iron catalysts require higher reaction temperatures than cobalt, i.e., in the range of 230-260°C.

This circumstance makes it impossible to carry out synthesis using iron catalysts in the units ordinarily used for cobalt catalysts, or those readily at hand. New synthesis furnaces must be used which make possible operation at temperatures of 230-260°C and at gas pressures of 10-20 atmospheres.

The procedure can follow the same course as with cobalt catalysts, i.e., with once through passage of the gas. The application of a gas circulation with recycling a portion of the end gas is not absolutely essential, but is to be recommended on account of some advantages. To be sure, in this case increased expense must be considered for the removal of the intermediately-formed products. With regard to yields and products formed, certain numeric items can be selected from the accompanying tables. The yields of 140 g./cu. meter gas can be guaranteed. Actually we obtained considerably higher yields, particularly for paraffin synthesis.

In contrast to the cobalt catalysts it is possible, using iron to modify the boiling range of the liquid products within very wide limits, so that, for example, primarily naphtha or paraffin can be obtained. A further difference from cobalt synthesis lies in the fact that the liquid products have a much higher olefin content, and are therefore more valuable as motor fuels and for further processing. Attention may be called to the fact that the paraffin obtained by means of iron catalysts is just as well suited for oxidation to produce fatty acid as the paraffin from cobalt synthesis.

II. Cobalt-Water gas-Recycle synthesis

With the existing installations, it has not previously been possible to increase the olefin content of the liquid products above a relatively low amount, because the cobalt synthesis produces only a little olefin and because in the available iron catalyst units, which produce more olefins, the operation conld not be carried out because of the high reaction temperature.

We have now found that olefin production can be appreciably increased in the existing synthesis plants, by changing from hydrogen-rich water gas to normal water gas and at the same time recycling a certain portion of the end gas. This change brings several disadvantages over normal cobalt synthesis operation. The operating costs are higher because gas pressure is increased, and the cost of recycling must be added. Certain equipment expenses must be incurred, particularly for the relatively large condensing apparatus which is required to remove the liquid products from the circulation system. The gas must be preheated and a lower vaporization must be considered. Another disadvantage is a certain increase in the content of oxygen-containing products.

Against these, there are certain advantages which are based on the extraordinary increase in olefin formation. This higher olefin content results first of all in a decided improvement in the quality of the naphtha. Moreover the olefins have proved to be highly suitable for lubricating oil manufacture so that the erection of a cracking unit becomes superfluous.

Finally about four times more olefins are obtained in the boiling range of heavy oil, which are particularly valuable for further chemical processing. The life of the catalyst is not affected by the change in operation.

Frames 270-271 are tables showing synthesis with cobalt catalyst, single pass and recycle iron catalyst synthesis paraffin naphtha.

ITEM 109. COMPARISON OF RECYCLING AND DIRECT SYNTHESIS

Frame 272-274, Influence of gas introduction
upon the synthesis. June 14, 1941

Results of tests with iron catalysts indicate:

1. Synthesis temperature with recirculation is always somewhat higher than with single pass operation, about 2-3 °C with a circulation of 1 + 2.5, and 5°C or more with 1 + 5 and higher.

2. Methane formation with direct pass is no higher than with medium recycle, and somewhat less than with high recycle.

3. Conversion of CO in a recycle of 1 + 2.5 is not appreciably different from that of direct synthesis, but it decreases with increasing recycle, for example 60% CO conversion at 1 + 2.5 and 55% at a recycle of 1 + 5.0.

4. Boiling range is definitely dependent upon gas introduction. In direct synthesis, optimum amounts of higher boiling products occur; with increasing recirculation, very low-boiling products are obtained.

5. The effect of gas introduction upon olefin formation is less marked. In general, more olefins are formed with increasing recycling.

6. The consumption proportion H_2:CO is dependent on the gas introduction in that, with increasing recirculation, the H_2 conversion increases above the CO conversion.

7. In order to have appreciable differences between the two methods of gas treatment, a recirculation of at least 1 + 1.5 must be applied.

8. It may be possible to adjust the CO/H_2 ratio at the most desirable point by regulating the circulation.

9. In two months operation, catalyst life seems to be somewhat shorter for direct passage than for recycle.

Frame 275, Cobalt recycle synthesis
December 20, 1941

There seem to be two disadvantages to the use of cobalt catalysts in recycle operation: 1. The capacity of the converter seems to be appreciably less, and 2. Paraffin production is also considerably lower.

ITEM 110. WATER GAS CONVERSION

Frame 276-277, Conversion. Oct. 6, 1941

A letter requests permission to study the effect of alkalized iron catalysts in water gas conversion, at temperatures which avoid the undesirable side reactions which occur above 300°.

Frame 278, Conversion. Aug. 23, 1941

It has been found that an iron-nickel catalyst is capable of converting water gas in the presence of steam, at a temperature of 200°C.

ITEM 111. METHANIZATION

Frame 279, Methane. Aug. 30, 1941

The following information has been gained:

1. Synthesis gas is smoothly methanized by nickel at 200°C with 6-fold charge.

2. Water gas and steam are methanized by Fe-Ni catalysts at 200°C and 5-fold charge.

3. Carbon monoxide over Fe, Ni with excess steam produced CO_2 and hydrogen almost exclusively, with traces of hydrocarbons, but with limited amounts of steam, good yields of liquid hydrocarbon are obtained.

A program for further study is proposed.

ITEM 112. INCREASING THE AMOUNT OF PARAFFIN WAX

Frame 280, Increasing paraffin.
April 14, 1943

Comments are made on suggestions for increasing the paraffin wax fraction in low-pressure synthesis. These include:

Decrease of the magnesium content of the catalyst or a change to pure thorium catalysts would probably not be successful.

The use of gases richer in CO has been tested repeatedly. A slight increase in CO-content does not result in any perceptible increase in paraffin.

The addition of ammonia to the synthesis gas will increase the paraffin fraction appreciably.

Frame 281-285, Increase in the paraffin
fractions in the products
of existing synthesis plants.
October 2, 1941

It had been proved in 1940 that the use of iron catalysts could increase the production of solid paraffin wax up to 64% and more. The present problem, however, concerns an increase in paraffins using existing equipment which precludes the use of iron catalysts.

Experiments have shown that the use of nickel or nickel-containing catalysts is not suitable for the production of large amounts of solid paraffins. Previous tests showed that high paraffin yields could be attained when highly concentrated cobalt catalysts were used. Thorium and manganese were used as activators. With such concentrated cobalt catalysts, paraffinfractions of 50-80% could be obtained. Catalyst life was six months and more.

Average numeric results are given for paraffin synthesis with concentrated Co-Th or CoMn catalysts on a pilot plant scale.

	Co/Th catalyst	Co/Mn catalyst
Soft paraffin (320-460°)	21%	22%
Hard paraffin 460°	33	42
Total paraffin	54	64
Temperature °C	175-178	165-168
Pressure (atmospheres)	10	10
Gas	Synthesis gas	Synthesis gas
Gas introduction	single pass	single pass
Gas charge	normal	normal
Contraction %	70	60
CO conversion %	85	65
CO as CO_2	0	0
CO as CH_4	10	11
CO degree of liquefaction %	90	89
H_2 conversion	87	68
$CO+H_2$ conversion	86	65
Yields:		
Gasol g./cu. meter gas	15	10
Liquid product	130	100
Total yield	145	110
Boiling range:		
Naphtha (up to 200°) wt. %	22	20
Oil 200-320°	24	16
Soft wax (320-460)	21	22
Hard wax 460	33	44
Total wax	54	66

ITEM 113. CONCENTRATED COBALT CATALYST

Frame 286, Cobalt catalyst
October 20, 1941

To increase wax production, the best composition for a concentrated cobalt catalyst is 100 parts Co, 15 parts ThO_2 and 15 parts kieselguhr.

Frame 287-289

- Detailed instructions for the preparation of cobalt catalysts.

Frames 290-291 consist of tables showing operating conditions and the results obtained with catalysts prepared according to the above instructions.

Frame 292, Concentrated cobalt-thoria catalyst. Oct. 11, 1941

Further figures are given on different amounts of catalyst and varying yields.

ITEM 114. IRON CATALYSTS, SCHWARZHEIDE, DEC. 22, 1941

Frame 293-295

It has been found that iron catalysts can be used for the production of naphtha as well as for obtaining paraffin. The operating conditions are: 15 atmospheres gas pressure, maximum temperature during a 3-month period, 220°C. An ideal gas consisting of pure CO and H_2, practically free from inerts, was used in the proportion of 1:0.6-0.8 CO/H_2. The synthesis was conducted in once-through operation with normal charge. The conversion amounted to about 80% of the CO, the gasification about 5.6%.

The average paraffin production during the run was about 70% boiling above 320°C, at times it was nearly 75%. The temperature still remained below 220°C when 80% of the CO had been worked up. No decrease in catalyst activity could be determined.

Of the fraction boiling above 320°C, about 25% was paraffin boiling 320-460°C, and 75% hard wax with a melting point of 105°C.

That a relatively high conversion was obtained at unusually low temperature may be ascribed to the comparative freedom from inert gases in the synthesis gas mixture.

ITEM 115 COMMENTS ON PATENT APPLICATION M 136921 OF METALLGESELLSCHAFT, JUNE 15, 1942

The comments are not favorable.

ITEM 116. FISCHER SYNTHESIS

Frame 299-314, The influence of the reaction
products upon the course of the
Fischer synthesis. May 11, 1942

A series of tests is described, where a recycle process was used. From the results of these tests, the following conclusions are drawn: A recycle system will effect a higher conversion, but never so high as a system where several furnaces are connected in series, with intervening condensation. The proportion between steam, conversion gas and inert gas is of importance in the effect on pressure, temperature and yield.

Frame 315, Fischer synthesis.
Sept. 8, 1942

This is a letter transmitting a report upon Fischer syntheses using cobalt catalyst.

ITEM 117.

Frame 316-317, Calculation of residual
volume of hydrocarbon
synthesis from composition
of gas. Feb. 12, 1944

Equations are given for the making of such calculations and for calculating and estimating the course of the synthesis.

ITEM 118. LOW TEMPERATURE TAR FROM GAS GENERATORS

Frames 319-324 are almost illegible

Frame 325-326, Report of conference
between Lurgi and
Ruhrbenzin. July 20, 1938

While experimental vacuum distillation has not been practiced at Lurgi, normal pressure distillation gave results which agreed with those of Ruhrbenzin. A special vacuum distillation of the Lurgi mixture of tar and middle oils was planned.

A program for slowly chilling and settling a tar oil mixture was in process. The paraffin was to be filtered and washed, CCl_4 was to be distilled off, the filtrate was to be deasphalted and treated with methanol.

Frame 327-339, Recovery of diesel oil and fuel
oil from Lurgi oils. July 28,
1938

The products from the dry distillation of coal were used as starting material. A mixture of 59.5% (Wt.) tar and 40.5% middle oil was distilled to coke at atmospheric pressure in iron stills.

~~Yield:~~

Naphtha (up to 200°C)	8%
Fraction 200 end	87
Coke, gas and loss	5

The fraction above 200°C (designated in this report as D200) contained 24% paraffin hardening at 40-42°C, and had the following properties:

d_{20} 0.89 coke 2.42%
hardening point 15°C asphalt 0.04%

A sample of the original mixture was vacuum stilled and gave about the same percent yield boiling above 200°C as the atmospheric pressure distillation, but produced practically no cracking.

The distillates were treated with normal refining agents, and also with selective solvents. A preferred method of operation is noted. Six sheets of tables and curves are given.

Frame 340-341

A letter transmitting a report on tar oil from Prosper. The report consists of a manuscript table.

Frame 342-345, Vacuum distillation of
Hirschfeld pressure gasification
tar, in the Frankfort pilot plant
of Lurgi. August 30-31, 1938

In order to determine the advisability of refining tars to produce diesel and fuel oils, a pressure gas tar was subjected to high vacuum distillation. The distillate was dewaxed and the wax-free oil separated by selective solvents in a raffinate (diesel oil) and an extract (heating oil).

The vacuum still is described and its operation. Properties of the topped oil are given. Experimental conditions are described, and the yield obtained. The results show that vacuum stilling tends to produce a good yield without coking.

Frame 346-348, Diesel fuel - Dewaxing
September 20, 1938

Proposals are noted for dewaxing with centrifuges if necessary at two temperature levels. Estimates are given as to the cost of such operation.

Frame 349-351, Bubiag tar. October 4, 1938

Frame 352-360, Working up lignite tar.
October 7, 1938

The Edeleanu firm is now a subsidiary of Deutsche Erdol A.G. It has plants for refining mineral oils by means of SO_2, and also for dewaxing oils and refining paraffin with SO_2. Frame 357 gives a flow sheet for a plant for dewaxing a tar oil distillate.

Frame 361-362, Refining brown coal tar
October 7, 1938

The properties are given of a tar which is to be sent to Edeleanu for treatment.

Frame 363-364, Tar refining. Oct. 19, 1938

This gives more discussion on dewaxing tars by treatment with SO_2.

Frame 365-366, Tar refining. Oct. 20, 1938

Frame 367-385, Recovery of diesel fuel and
furnace oil from brown coal
tar oils. Dec. 12, 1938

This report discusses: I. Dewaxing of "ERR" tar using acetone and a benzolethanol-methanol mixture; II. Treatment of total product boiling above 200°C; III. Treating to obtain a maximum yield of fuel oil; IV. Refining and desulfurizing the light oil. There are 11 pages of charts, tables, and flow sheets.

Frame 386-388, Analyses of samples of light oils
from tar from Bollen. Dec. 1, 1938

Frame 389-396, Investigation and treatment of
pressure gas tar and naphtha from
Falkenau coal. Nov. 29, 1938

A. Tar. The tar contains about 10% water, 8.7% naphtha insoluble, 1.4% benzol-insoluble, 6% paraffin and appreciable amounts of creosotes. Refining to obtain diesel oil can be effected by mixing with a diesel oil fraction 200-250°C, distilling the mixture, dewaxing at -20°C and further processing; or the dehydrated tar can be distilled to coke, the distillate mixed with a diesel oil fraction, dewaxed, and caustic-treated.

B. Naphtha. The naphthas are highly aromatic, and may be used to improve the octane numbers of motor fuels.

Frame 397-398, Investigation of a crude tar
from the Bubiag direct flow
plant in Ruhland. June 20, 1939

A sample from the Braunkohlen- and Brikett-Industrie at Berlin was studied for evaluation of its use in diesel fuel and furnace oil. Neither the tar nor the fraction boiling above 200°C is suitable for use as a direct constituent of a diesel fuel. Further refining is needed.

Frame 399-401, Tar from destructive distillation
plant at Falkenau. July 13, 1939

This tar was distilled in the laboratory, using an iron still, at normal pressure. The distillate above 200°C was dewaxed with acetone and then caustic-washed to remove phenols. It is possible to prepare a diesel fuel from this distillate.

ITEM 119. ADDITION OF ESTERS, ACIDS, AND SOAPS TO LUBRICATING OILS

Frame 403-406, Investigation of ester oil
E1 from the Research Labor-
atory RCH. July 6, 1943

Esters were prepared from the fatty acids and alcohols of the diesel oil fraction from Ruhrchemie primary products. These esters showed a very flat viscosity-temperature curve, and their use as additives to lubricating oil was tested, to see how the viscosity-pole height might be affected. Oils to which 33% ester had been added were tested for wear, oil consumption and aging, as well as piston attack and pumping characteristics. Sample E1 proved to be quite satisfactory at increased operating temperatures. Oil consumption was increased because of lowered viscosity. Two pages of tables are given.

Frame 407-409, Proposal for patent application
on lubricating oil carboxylic
acids. Aug. 31 1942

Claims:

1. Lubricants which contain carboxylic acids or their derivatives, characterized by the fact that these acids consist in part or entirely of lubricating oil acids.

2. Lubricants according to claim 1, characterized in that lubricating oil carboxylic acids contained therein have been produced by the attachment of carbon monoxide and hydrogen to olefinic hydrocarbons with lubricating properties, with subsequent conversion into the carboxylic acids or their derivatives.

Lubricants containing carboxylic acids have been known, for instance mixtures of lubricating oils and metal salts of fatty acids. In all these cases, however, the constituents with actual lubricating qualities differ essentially, with regard to their chemical and physical behavior, from carboxylic acids whose molecules show no lubricant structure.

This invention relates to lubricants in which the carboxylic acids have a structure which is entirely or partially similar to that of the lubricating constituents. Such acids are derived from hydrocarbons with lubricating properties, by the incorporation of one or more carboxyl groups and are hereinafter designated as lubricant carboxylic acids.

Lubricant carboxylic acids can be obtained, for example, by the catalytic addition of carbon monoxide and hydrogen to olefinic lubricating oils, with subsequent oxidation of the resulting aldehydes. These lubricating oil aldehydes can also be reduced to alcohols and the latter converted into lubricating oil carboxylic acids in the customary manner by caustic fusion. As initial materials it is advantageous to utilize synthetic lubricating oils such as are produced by the polymerization of olefin hydrocarbons with $AlCl_3$, BF_3 and the like.

These lubricating oil acids can be isolated as such or converted into the desired derivatives such as esters or amides and these latter added to the lubricants. However lubricating oil acids can also be converted into the desired derivatives in the presence of the lubricating oil fractions not converted with H_2 and CO, and the desired lubricant mixtures can be obtained in this way, without the necessity of separating the acids from the unconverted fractions. Two examples of proposed lubricant compositions are given.

Frame 410-411, Synthetic lubricants
April 10, 1941

A proposed patent application.

It has long been known that consistent lubricants can be made by bringing lubricating oils and soaps into intimate admixture with one another. Heretofore, however, only such soaps have been used as were prepared from fatty acids having a chemical structure which differs from that of the lubricating oils. For example the normal straight-chain aliphatic fatty acids are used in the molecular range from C_{10} to C_{20}, such as are normally used in soap manufacture.

In contrast to this, the lubricants prepared according to this invention contain soap fractions whose fatty acids posses the same or a similar chemical structure to that of the lubricating oil fractions. The difference between the lubricating oil molecule and the fatty acid molecule then consists merely in the added carboxyl group. It can be readily understood, that, in contrast to previous consistent lubricants, the fatty acid molecule can here contribute to the lubricating effect, because of its lubricating oil structure.

Such compounded lubricants can be advantageously produced by starting with lubricating oils which are more or less unsaturated. To these unsaturated bonds, carbon monoxide and hydrogen are first catalytically attached in the known manner, resulting in the formation of the corresponding aldehydes. These aldehydes can then be oxidized with air, and the resulting fatty acids saponified by reacting with metal oxides, hydroxides, or carbonates. In this way consistent lubricants can be prepared which consist of a mixture of lubricating oils and lubricating oil soaps of the various metals such as the alkalies, alkaline earths, aluminum, lead, iron, zinc etc.

Or the aldehyde lubricating oil mixture, obtained by water gas reaction with the original lubricating oil, may be hydrogenated to the corresponding alcohol-lubricating oil mixture, and this mixture may be subjected to alkali fusion. Consistent lubricants are then produced which comprise a blend of lubricating oils and lubricating oil alkali soaps. These mixtures can then be converted into those which contain other metals such as the alkaline earths, aluminum, lead, zinc, iron, etc., instead of alkalies.

Any excess alkali present in the alkali melt can also be neutralized with fatty acids from other sources. The aldehyde may also be converted directly with alkali, without preceding hydrogenation.

Finally the lubricants obtained according to this invention can be mixed with larger or smaller portions of consistent lubricants or with soaps of other origin, in order to modify their properties.

Frame 412-418, Studies of oils from BVA treated with CO and H_2. Mar. 30, 1939

Tests were made on two small samples to determine the effect of treating on oxidation stability. Three tables and two sets of curves report the results.

ITEM 120. ALKYL BENZOLES

Frame 419-420, March 14, 1936

The Deutsche Versuchsanstalt für Luftfahrt has definite need for fuels to be tested. Propylbenzol samples were submitted but tests were not complete. Among the requirements are high antiknock, high stability in the cold, and low iodine number. The organization desires prompt delivery of larger samples of various oils.

ITEM 121. TRANSFORMER OILS

Frame 421-427, Electric insulating oils. June 22, 1936

A letter from Steinmann gives a brief discussion on the tests of a sample of synthetic oil proposed for use as a switch or transformer oil. The oil was satisfactory in some tests, but was too sensitive to changes when exposed to air and heated. A synthetic oil for use as a cable saturating insulator, for high voltage work, is needed; this should be a more viscous product with about the following properties:

Sp. gr.	0.935 at the highest
Engler viscosity	50° at 50°C
	3-4° at 100°

Flash point above 250°C

Free from acid and resins, no asphaltenes.

Tar formation number, less than 0.1%

Three questions are asked:

1. Can a mobile synthetic transformer or switch oil be prepared which has adequate age stability?
2. When can an improved sample be sent for testing as to dielectric quality?
3. Can a heavy, viscous oil be prepared from Fischer-Tropsch products, suitable for use as a cable impregnating oil?

Frames 424-427 give the report of the Physical Technical Testing Laboratory on a sample of insulating oil from Ruhrchemie.

About 8 kg. of a bright yellowish transformer oil came in container #99. The sample has an odor of mineral oil, it is transparent and clear in a film 10 cm. thick at 20°C. No solid material was present.

Sp. gr. 0.842 at 20°

Viscosity

Temperature	Viscosity Engler	centistokes
20	6.36	47.9
5	15.5	117.9
0	22.0	167.4
-5	31.9	242.5

Hardening point, below -15°

Flash point 150°

No free mineral acid, resins tar oil, saponifiable fat, water or water-soluble ash are present.

Saponification number, 0.13

Aging Tendency

The tar formation number is too high, and traces of insolubles are formed after heating 70 hours to 120°C and introducing oxygen.

Electrical tests

A breakdown test was made between two copper balls; the resistance of the oil as received was $120 kV_{eff}/cm$.

This oil corresponds to the minimum requirements. Dielectric loss is stated.

ITEM 122. ANALYSIS OF DIESEL OIL, AUGUST 21, 1926 (FRAME 428)

ITEM 123. NITRATION OF DIESEL OILS IS NOT IN THIS REEL, BUT IS TO BE FOUND AT THE VERY FIRST OF REEL 46.

ITEM 124. CONFERENCES AT THE SYNTHESIS WORKS, ESSEN, OCT. 3, 1941

Frame 430-431

List of participants, brief report on the status of research and a list of papers to be presented.

Frame 432-440, Recent Experiments in Fine Purification by Dr. Pranschke

In the course of our exploratory work concerning the fine purification of synthesis gas, we at Schwarzheide arrived at a conclusion which will be described here today, even though in many respects it still appears to be experimentally and operatively not yet fully matured.

We have found that by enlarging the pore volume of the fine purifier catalyst from 50% to around 70%, an appreciably better removal of organic sulfur can be achieved than heretofore and that this increased purification effect begins at temperatures which lie on an average 60-70°C. lower than when using the purifying masses heretofore customary.

We must emphasize, to be sure, that our experiences refer in the first place only to the organic sulfur in the synthesis gas at Schwarzheide which is known to be prepared from brown coal briquettes in Koppers and Didier installations, freed from dust by electrofiltration, freed from hydrogen sulfide in a dry purifier and finally fine purified.

With the total sulfur content of 0.5-0.8% in the brown coal, of which about 50-60% is present as volatile sulfur, our synthesis gas before fine purification still contains about 2.5-3.5 g. organic sulfur per 100 cubic meters.

Compared with other synthesis works, this content or organic sulfur is not high but its composition is very complex.

Besides carbon disulfide and mercaptans, a number of aromatic sulfur compounds have been identified such as thiophene, thionaphthene and the like. Furthermore, we know that a notable fraction of residual sulfur is present whose constitution is unknown.

There is the additional fact that our synthesis gas contains condensates whose presence makes fine purification difficult.

Under these conditions and using the previously customary purifying masses, it was not possible to arrive at values below 0.2 g. organic sulfur per 100 cubic meters synthesis gas with the desired uniformity of product.

This fact was the incentive for a large number of laboratory and works experiments, in which however, important improvements could not be achieved.

An indication toward possible success was obtained only, when in the course of comparative experiments with coarse-grained masses having a grain diameter of about 10 mm. and fine grain masses with a grain diameter of about 2 mm., we investigated more closely the fine granules. Herein we found that by the comminution of the coarse grain to about 1/5 of its diameter, not merely one but two properties had been altered. In addition to the surface, the pore volume had increased by 10%.

At first we did not know to what we could ascribe the better purification action of the fine grain which had been shown in the above mentioned experiment.

With the comprehensive investigations then initiated concerning the question of porosity, we soon saw that as high as possible porosity of the contact mass was of decisive significance for fine purification.

Before the preparation of special highly porous masses is described, two facts must be pointed out: (1) if the Lauta contact with 50% water that is the starting material for the preparation of our fine purifying mass is dried down to a water content of about 0-4%, then a grain is obtained with a porosity of 80-85%, (2) if from the same Lauta contact fine purification masses are prepared in that, according to the previous customary methods, moist Lauta contact is mixed with calcined soda, we obtained a grain with a porosity of only 45-50% and 55% the highest.

Accordingly a new way must be sought to avoid this loss in porosity or to limit it to a tolerable amount.

The Lauta contact itself, with a porosity of 80%, showed excellent results in fine purification tests in the laboratory but its use did not at first seem desirable in general operations since the hardness of its grain at 80% porosity amounts to only 1.7 kg/cm^2, and further because its alkaline content is too small or varies too greatly; it lies within the limit of 2-12% but usually around 5-8%.

In order therefore to obtain fine purification contacts with this higher alkaline content and with finer grain, we were forced to mix the Lauta mass with soda.

If, in this operation, as had previously been customary, fine grained calcined soda was introduced into a Lauta contact with 50-60% water and the mixture stirred, an appreciable development of heat took place because of the reaction between soda and water, the mixture assumed a pasty of heavy liquid consistency, the grain structure of the Lauta contact was completely lost, the porosity dropped about 30%.

If, on the contrary, in the preparation of the fine purifying contact, the occurrence of the pasty or liquid state of the soda-Lauta mass mixture was avoided, then it was very easily possible to produce masses with porosities of 70%, for example. For this purpose it was only necessary to control the reaction of the calcined soda with the water of the Lauta contact.

This is accomplished in a simple manner if the soda is mixed previously with a suitable amount of pre-dried Lauta contact, that is, if it is first diluted and only then brought into contact with the remaining wet mass.

The complete procedure is as follows:

100 kg. of Lauta contact with an alkali content of 2% and a water content of 50% are divided into two portions, portion 1 is dried, mixed well with about 5 kg. of soda and then added to portion 2.

The crumbly mixture obtained, which contains about 25% water, is moistened by spraying with a water mist on the surface until a moldable consistency is obtained, then pressed through a wing press for molding passed through screens and finally dried.

The drying occurs preferably in two stages in that first at 60-80°C the mass is pre-dried for hardening; the drying is then completed at a high temperature. There is produced from this 55 kg. of fine purified contact with about 15% alkali and at least 70% porosity whose grain hardness of about 3-4 kg. per square centimeter is sufficient for the operation. In this example an alkali content of 15% is mentioned because experiments had shown that alkali contents of this order of magnitude are most favorable.

The comparison of characteristic index numbers of the new fine purifier mass and previously prepared mass is shown in the following:

(Table on Frame 435)

	Shatter Weight	Grain hardness	Soda	Fe_2O_3	Porosity
Previous mass	0.7	6-7 kg./cm²	30%	36%	50%
New mass	0.5	3-4	45%	44%	70%

These figures show appreciable differences.

For a more detailed explanation of these differences, figures from a comparative experiment with old and new masses will be given here using two fine purification units of the same construction.

(Table on Frame 436)

	Total charge of purifier	Alkali calc. as soda	Iron calc. as Fe_2O_3
Old mass	100.8 tons	29.5 tons	36.7 tons
New mass	76 tons	12.5 tons	33.8 tons

It is evident that in using the new fine purifier mass, savings of Lauta contact and soda result per volume unit of the fine purifier.

Against these advantages of lower shatterweight and soda content of the new mass, there is the disadvantage of its lowered grain hardness.

Here too a few figures from operating experiments are available. We loaded two railroad cars with highly porous mass and unloaded them again, and then weighed the amount of dust of 0-6mm grain diameter.

We obtained here 13.8% and 17.0% dust respectively. In a comparative experiment with old contact mass, under like conditions we obtained 8.9% and 8.7% dust of the same grain size.

Summarized, from the comparative figures of the shatter weight and the grain breakdown of the masses it is evident that with one ton of highly porous fine purification mass about 20% more of purification space can be filled than formerly.

The porosity of the new mass amounts to 70%, that is the internal surface of the iron compounds presented to the gas during purification is about 40% higher than in the case of a mass with a pore volume of only 50%.

It makes no difference here that the total amount of iron in the fine purifier is about 8% lower than formerly, since according to our operating results in Schwarzheide fine purifier masses on the average can be saturated only up to about 10% with sulfur because above this other influences such as carbon deposit, crusting of the surface by condensate residues and the like, make the masses prematurely unsable. The purification results obtained up to the present time with the new masses confirm this opinion.

In a laboratory experiment of over 8,000 hours duration, in which masses with 50% and with 70% pore volume were compared at equal temperature and load, we found in the mass with 50% pore volume a residual content of 1.0 g. organic sulfur per 1000 cubicmeters of gas corresponding to a work-up of 70% of the total sulfur, while the mass with a pore volume of 70% absorbed the organic sulfur up to 96.8% and allowed only 0.1 g. organic sulfur per 100 cubicmeters of gas to pass through. Both experiments were made with only one purifying tower, a simplification which we frequently use in the laboratory in determining the usability of fine purifying masses.

We very soon determined in addition that such good purification effects could also be obtained with the new mass at lower temperatures than had previously been customary in fine purifications.

The latter fact is significant in many ways. There is a saving of heating gas, the apparatus is spared and injurious side reactions of the synthesis gasses are avoided, for example, deposition of carbon, reforming of condensate which previously have been observed in the fine purification within the temperature range from 230-320°C.

With regard to the question of the temperature drop and simultaneous better fine purification of the synthesis gas, two operating tests may here be disclosed which, to be sure, are not yet concluded but which have many quite significant figures.

In one comparative test with old and new mass, during a running time of 100 days up to the present, the following average temperatures and average sulfur values have been obtained:

In mass I with 50% porosity, the average temperature was 200°C. in the A tower and 187°C. in the B tower, with the new mass II 164°C in the A tower and 158°C. in the B tower. In spite of this with equal charge and gas characteristics, the average sulfur value was 0.21 g. per hundred cubicmeters after mass I and only 0.9 g. per hundred cubicmeters after mass II.

For the first time it was possible in Schwarzheide to obtain average sulfur values below 0.1 g. per hundred cubicmeters of gas in operation.

Still more significant is the superiority of the newer mass in an operating test of more recent date, in which a fine purification system was operated at 80°C, that is at a temperature of about 100°C. lower than was heretofore customary.

After a running time of 23 days the highest sulfur value heretofore obtained in purified synthesis gas was 0.11 g. per 100 cubicmeters, the average sulfur value was only 0.06 g. per 100 cubic meters, the average temperature in the A and B towers were 87°C and 81°C respectively.

Unfortunately, concerning this test - which is intended particularly to show the high activity of the new mass, - we can report only concerning an operating time of 23 days; however, the figures here given are already very significant.

We know that appreciably more information must be collected before a final decision is possible concerning the new fine purifying mass; however, advantages are already shown so clearly that there is a well grounded hope that the sulfur value in the Schwarzheide synthesis gas may be lowered with the new mass, down to partial pressures which are not injurious for the synthesis catalyst.

Discussion follows:

The inquiry of Ritter as to whether these porous masses had been used for a purification of a gas with high sulfur content was answered in the negative. However, experiments are under way at Lutzkendorf which cannot as yet be reported.

Feist inquired whether during operation the attrition of the new mass is not appreciably higher than with normal contact and at the same time the greater hardness is stated to be lower. Attrition is probably higher but no operating difficulties have resulted from this cause.

To Braun's question the charge of an aggregate prepared with the new mass is stated to be normal, that is 14-15,000 cubicmeters per hour and the oxygen addition is 0.4 volumes prior to fine purification. This oxygen addition is necessary in Schwarzheide although 0.2-0.3% oxygen remains in the synthesis gas after fine purification. Any effect upon the synthesis contact has not been observed. In small scale experiments it was proved that only oxygen contents of more than 0.5% are injurious. These observations are confirmed in the experimental results in the Chemische Werke, Essen Steinkohle and Ruhrbenzin.

Schwenke stated that at present an activated charcoal for preliminary purification of synthesis gas before fine purification is planned at his plant and that at the end of the year probably observations concerning this pre-purification will be available. Schwenke inquired whether the installation of an activated charcoal plant for a removal of condensate fractions is still under consideration at Schwarzheide. Hochschwender answered this in the negative since the sulfur purification now attempted no longer makes this question seem so urgent as it had been a short time ago. Feist inquired whether with the condensate proportions in the synthesis gas at Schwarzheide, anything had changed through the utilization of the new contact. Francke believed that a decrease could be shown but investigations on this are still in process. It is intended that complete reports will be made on this matter later.

Martin inquired whether highly porous masses should be introduced in both towers of a fine purification system, or in the first tower normal masses and in the second tower the new masses, and whether the new mass is appreciably more expensive in the cost of production. Hochschwender and Kollmar explained in this connection that a two-stage method of operation is not intended and that on the economic side no firmly binding statements can as yet be made. It is, however, proposed that somewhat higher costs of manufacture and an increase in price because of the lower load possibilities ~~may be equalized through the lessened soda content and through a saving of~~ heating gas because of the lower operating temperatures if they are not exceeded.

Grimme proved that in operating fine purification with the customary addition of oxygen, the sulfur is combined as sodium sulfate. ~~He believed therefore that with a lowered sodium carbonate addition in the~~ new mass, the saturation limits of the mix must be lower. In Schwarzheide up to now the saturation limits of the mass have not yet been investigated from this view.

Lopmann believed that the different behavior of many fine purifier systems could be traced to inequalities in the fine purifying mass. Above all, variations in porosity were proved. Martin explained these variations by the changing quality of the substance which served as the raw material, which varies sharply, particularly in its moisture because of storage in the open air, which is at present the only possible storage. A reexamination of this question is promised.

Weitenhiller showed that the higher the loading of a single system is maintained so much the better complete saturation of the mass can be achieved.

Kowalski stated that at Schaffgotsch the removal of organic sulfur (15 g. per 100 cubicmeters synthesis gas) down to 0.1-0.15 g. per 100 cubic meters is successfully accomplished, and a complete saturation of the contact mass is achieved. Here also it is thought that the sulfur is combined with the sodium carbonate. Any combination with the iron could not be proved.

The inquiry of Weitenhiller as to whether the high porosity mass can also be delivered to other plants was answered in the negative, since in the scope of the supply program, the entire production, at least until the end of the year, is allotted. According to this program the Lutzendorf Werke is the only foreign plant which is supplied.

Frame 441-447, Influence of high sulfur
content upon the synthesis.
By Dr. Mobry, of Krupp
Treibstoffwerk.

The heat exchangers in the fine purification unit did not function properly and as a result it was impossible to maintain the sulfur content within the desired limits. This caused a decrease in catalyst life; attempts to improve performance by increasing the temperature caused a greater formation of methane. An equation for determining the amount of excess sulfur as compared with catalyst efficiency is given. Two figures, one a block chart and the other a set of curves, indicate the relationship between specific yield and sulfur load over a period of about eight months.

Frame 448-457, Formation of hydrogen sulfide
in synthesis gas, from the sulfates
in the cooling water in direct gas
coolers. Dr. Feisst, Ruhrbenzin.

An undesirable formation of hydrogen sulfide occurred during the preparation of synthesis gas. This was particularly troublesome in preparing the gas for medium pressure synthesis. It was found that a definite increase in sulfur content occurred after the gas had passed through a cooling tower in direct contact with cooling water which contained a certain amount of sulfates. The presence of a sulfur-converting strain of bacteria was suspected, and later confirmed.

Operating conditions were highly favorable to the growth of such organisms. The addition of zinc chloride to the cooling water was effective in checking the bacterial action. It was noted that plants of other companies had difficulties which might be traced to the action of sulfur-reducing bacteria.

Frame 458-463, Development of the pressure synthesis to the olefin synthesis.

By. Dr. Dahm, Ruhrbenzin

When in 1936 a plant was erected for the production of motor fuels from carbon monoxide and hydrogen, it was felt that the process would insure the provision of supplies of mineral oil. The chemistry of the aliphatic hydrocarbons promised a field as important as that of aromatics from coal distillation. Since the unsaturated aliphatics were a desirable raw material for synthesis operations, a definite effort was made to produce these unsaturates.

An increase in the CO concentration favors the production of olefins, but in low pressure operation, increasing the CO concentration beyond a definite limit causes difficulties with the catalyst. If the gas is diluted by recycling, these difficulties may be overcome, but the large volume of gas required necessitated the construction of extremely large and expensive equipment. The unsaturated hydrocarbons produced have a relatively low boiling point. However, the unsaturates which are of chemical interest are those of higher boiling range.

It was then found that a comparatively small increase in operating pressure would have decided influence on the nature of the hydrocarbons; accordingly plants were constructed to operate at medium pressure. The products from this type of operation were of much greater interest than those of normal pressure synthesis. The primary products of medium pressure synthesis were paraffinic in nature, but were an excellent initial material for thermal cracking to product olefins. Medium pressure synthesis in its present stage can be considered as a step in the olefin synthesis operation.

Operation at medium pressure showed that the gaseous component required a different manipulation from that of normal pressure synthesis.

The reaction in normal pressure synthesis may follow the course

$$1\ CO + 2H_2 = H_2O + CH_2$$

which would result in a decrease in the H_2 content of the residual gas, however it is probable that part of the gas reacts:

$$2\ CO + H_2 = CO_2 + CH_2.$$

In medium pressure syntheses, the reaction apparently follows equation 1 almost exclusively, so that much less CO_2 is formed. Charging CO and H_2 in the proportions of 1:2 does not afford sufficient hydrogen to achieve complete conversion of the CO. It was found necessary to introduce more water gas, with a larger proportion of hydrogen, at later points in the operation. The proportion is about 1:2.2.

A 2-stage operation was carried out at Ruhrbenzin for 1½ years, then a 3d stage was added. By starting with a gas containing 60% hydrogen in the first stage, a mixture of 1:1.55 was added when the initial ratio dropped; in the second stage a mixture of 1:1.65 and in the third of 1:1.75 was added. This resulted in a final ratio of 1:2.10. By this means, almost complete conversion - namely 94-95% - was attained with very little gasification.

Since the residual gas consisted largely of inerts, especially CO_2, a scrubber to remove this material was inserted after the converter gas compressor. While a small portion of reactive gas was also scrubbed out, the loss was counter balanced by the advantage of higher conversion.

This multi-stage process results in a considerable increase in olefin production. This can be still further increased by changing to the use of water gas.

Experiments showed 70% olefins in the naphtha fraction, up to 200°C, 45% in the oil fraction 200-320°C.

Contact chambers were the usual double tubes, gas pressure 10 atmospheres, temperatures at which optimum conversion is obtained vary somewhat, but an end temperature of 225°C is sufficient. The catalyst was the regular cobalt catalyst and catalyst life is somewhat longer than previously.

The primary products from this type of synthesis can be further worked up in various ways, to produce high-octane aviation gasoline, lubricating oils, fatty acids or other derivatives of the aliphatic series. In all cases, the olefins are the carriers of the reaction.

Frame 464-479, Advances in medium pressure synthesis
By Dr. Ohme, Hoeschbenzin, G.m.b.H.

By changing reaction conditions, particularly with reference to the $CO:H_2$ ratio, and by adding a third stage to the conversion, it was possible to increase the yield of liquid products by about 15%.

It has proved desirable, in the interests of product quality, to maintain the $CO:H_2$ ratio at about the same order of magnitude in all stages of a 3-stage operation. The use of a pressure scrubber, to remove excess CO_2 from the converter gas before it is introduced into the later stages, has proved highly desirable.

Frame 480-487. The carbon monoxide - hydrogen balance
as an aid in synthesis control.
By Dr. Grimme, Treibstoffwerk Rheinpreussen.

At present carbon balances are generally used for the control of operating relationships in practically all synthesis plants. The plant at Brabag utilized such calculations quite early, while work at Schwarzheide showed definitely that the amounts of carbon introduced into the syntheses and the amounts of carbon removed from the system as reaction products, including residual gas, are in agreement with each other.

This seems to be a self-evident fact, whose confirmation nevertheless causes difficulty even today in some plants.

However after Schwarzheide obtained the positive result that the weight of the carbon in the liquid, solid and gaseous products removed coincides with the weight of convertible carbon in the feed gas, we now have a simpler method for determining the yield of reaction products by calculation, from the decrease in convertible carbon, instead of by measurement. As convertible carbon is assumed only the carbon in the carbon monoxide and the carbon in any unsaturated hydrocarbons added. The carbon present in CH_4 and higher saturated hydrocarbons and in CO_2 is not considered as convertible.

Under this hypothesis, which is no longer questioned, by means of exact gas analysis of synthesis gas and natural gas samples, definite predictions can be made to the specific yields of gaseous and liquid products, and as to the course of the reaction during the synthesis.

In this way the control of the individual furnaces for each stage of the synthesis can be accomplished either by itself or in combination with the entire battery.

The validity of the data thus determined is dependent upon the sampling of the gases and the correct and carefully detailed determination, during the gas analyses, of the individual constituents of the gases.

In the type of balance calculations which we selected, the synthesis gas and the end gas in all cases were tested when cooled, before the separation of naphtha. In controlling individual furnaces, this is the only possibility, but even when controlling entire synthesis stages we prefer sampling the end gas rather than the residual gas.

The time required for sampling, for the sake of the uniformity of two parallel samples, should not be too long, and is limited to tests of 6 to 8 hours. If longer operating periods are to be controlled, a division into individual samples is recommended, with subsequent mixing of the individual samples to obtain a collective sample.

The volume of gas samples required is dependent upon the nature of the analytical method selected. It is not necessary, here, to go into the details of the analytical method which is based on the principle of Podbielniak distillation with severe refluxing of the condensed gas. For each ultimate analysis, we require about 100 liters of gas in which CO_2, H_2, CO, CH_4, N_2, C_2H_4 and C_2H_6, and perhaps also the C_3's and C_4's are determined. The content of aliphatic hydrocarbons in the end gas samples is not determined.

For the purpose of calculating a balance, however, it is absolutely necessary to include the fractions of the gaseous constituents which are dissolved in the condensate.

The experimental errors for constituents present in greater concentrations can be maintained within the limits of 0.2% by volume, as control measures have proved.

For constituents present in lower concentration, such as methane, ethane, propane and butane, the variation must be correspondingly lower.

On the basis of such analyses of parallel samples, the following calculations can be derived:

From the N_2 content is developed the contraction, or the amount of end gas which remains for each unit of volume of the synthesis gas after the reaction.

From the appropriate amounts of synthesis gas and end gas, and the CO-values of two samples can be calculated the total CO conversion. Furthermore the CO_2, CH_4 and C_2H_6 formation can be calculated for each unit volume of the synthesis gas. The amount of ethylene, which according to our observations always comprises only a small percent of the ethane formation, is included in the ethane calculation.

The weight of carbon which is contained in the volumes formed of CH_4, CO_2 and C_2H_6, is calculated and converted to the corresponding volume of CO.

After subtraction of these amounts of CO consumed in the formation of methane, carbon dioxide and ethane, from the total CO introduced, the remainder corresponds to the CO volume which was consumed in the production of hydrocarbons from C_3 upward.

By multiplication of the factor 0.634, long since introduced, there is obtained from this volume of CO the amount by weight of higher hydrocarbons formed, including gas. Variations in the average molecular weight of the hydrocarbons formed and in the olefin content, scarcely affect the magnitude of the factor named.

The correctness of this factor is shown by the good agreement with the calculated yields evidenced, when compared with actually measured yields from operations in repeated control experiments.

The suitability of yield determination by calculation can be increased still further when, in addition to the CO balance, a hydrogen balance is derived from the analyses in the same manner.

Hydrogen is consumed in the formation of methane, ethane and higher hydrocarbons, in proportions varying widely from those of the CO which is converted at the same time.

Furthermore the simultaneous formation of hydrogen throughout the conversion reaction must be taken into consideration; this can be recognized by the formation of CO_2.

In general, aside from the synthesis reactions, hydrogen can participate in the following reactions:

1. $CO + 3H_2 \longrightarrow CH_4 + H_2O$
2. $2CO + 5H_2 \rightarrow C_2H_6 + 2H_2O$
3. $CO + H_2O \rightarrow CO_2 + H_2$

Methane formation according to 1), and conversion according to 3) can be combined into the reaction:

4. $2CO + 2H_2 \longrightarrow CH_4 + CO_2$
5. $O_2 + 2H_2 \longrightarrow 2H_2O$

From these equations, on the basis of the amounts of methane, ethane and CO_2 formed, it is possible to calculate the consumption of hydrogen in the side reactions and to subtract that amount from the total hydrogen consumption, in order to determine by difference the amount which is required for the formation of higher hydrocarbons.

In order to calculate from this volume of hydrogen converted to higher hydrocarbons and water, the corresponding amount by weight of hydrocarbons formed, including gas oil, we apply the factor of 0.302 g product for each normal liter of converted hydrogen. This factor is valid for our conditions, where the mean molecular weight from C_3 to hard paraffin corresponds approximately to C_5 and the average olefin content is about 24%.

For other synthesis proportions, alterations in the above named factor are indispensable.

Yield measurements carried out over several months' time from the consumption of CO and H_2 show excellent agreement between the yields. Variations in the calculation of specific yield do not in general exceed the value of 1 g. products for each cubic meter of synthesis gas.

For the proper calculation of useful primary products from CO or H_2 consumption there is required in general for accurate analysis only the determination of CH_4 and C_2H_6 in the total hydrocarbon mixture.

When additional individual hydrocarbons are included, the possibility for further predictions is increased widely.

The added determination of C_3 and C_4 hydrocarbons can be accomplished without the expenditure of much time or trouble.

From this is developed the weight content of gas oil in the end gas, or in considering the contraction, the yield of gas oil for each unit by volume of synthesis charged.

Subtraction of this gas oil from the total yield of primary products determined by calculation of CO- or H_2 balance leads to the yield of liquid hydrocarbons (including paraffin). Double control of the reaction progress calculated from the CO balance and the hydrogen balance makes the conclusions derivable from such calculations appreciably more reliable. Some experiences obtained in several analyses will be described in more detail.

In cases where the contractions, determined from nitrogen do not agree with contraction indicated by gas contraction, it can be decided, by applying the H_2-CO balance which type of contraction is more nearly correct, since only when the contraction is correctly based can an agreement be reached between the two yield calculations from CO and H_2.

The good results of the hydrogen balance calculation prove that only elemental hydrogen participates in the reaction in the contact furnace, and no entrained hydrogen compounds in the synthesis gas, particularly none of the steam reacts. This finding holds true at least for our prevailing steam concentrations of 24-40 g in synthesis gas I, and 40-50g in synthesis gas II.

For the CO conversion which unquestionably takes place, and which can be recognized by the regular formation of CO_2, the water formed during the reaction must be held responsible.

Since the hydrogen consumption stands in the proportion of 2.1:1 to the CO consumed in the formation of aliphatic hydrocarbons, this leads to the recognized shifting of the $CO:H_2$ ratio in the end gas, as contracted with the synthesis gas. The drop in the proportion is certainly further influenced by the side reactions of the synthesis, where CO-conversion causes hydrogen formation, thereby checking the accelerated decrease in hydrogen.

In our operations, where in stages I and II together about 18% of the CO introduced is converted into gaseous products exclusive of gasol, i.e. 5% into CO_2, 11% into CH_4 and 2% into C_2H_6, a decrease occurs in the $CO:H_2$ ratio of 1.98 in the synthesis gas and 1.3-1.4 in end gas II.

This sharp decrease is completely confirmed in calculating the amount of hydrogen which is required for the production of the individual reaction products formed.

In case the decrease from normal $CO:H_2$ proportion in synthesis gas to the proportion in the end gas is less severe, it must be concluded that in such cases the formation of CO_2 and perhaps other side reactions must play a more important part than at our installation.

By applying the calculation of CO and H_2 balance to simultaneously-collected samples of gas from stage I and end gas stage II, the reaction relationships for each stage can be followed in detail.

In this case also additional measurements of gas can be neglected in the calculation.

Since in our method of connecting the two stages without an intermediate naphtha separator, it is impossible to obtain a direct product measurement for each stage, it was only through a balance calculation that an accurate control of the individual stages was possible for us. Through numerous comparative measurements in our plant, it is clearly shown that the total conversion in the second stage is just as great as in the first stage.

To be sure, a certain shift occurs between conversion to useful products and conversion to gaseous byproducts, and we have observed a somewhat greater formation of gaseous products in stage II.

With a yield of useful primary products (including gasol) in the first stage amounting to 130 g/cu. meter ideal gas, the yield in the second stage amounts on the average to 127 g/cu meter ideal gas.

Here the $CO:H_2$ ratio drops in the first stage from 2 to 1.8, and in the second stage from 1.8 to 1.3.

Probably the somewhat poorer liquefaction is caused by the unfavorable $CO:H_2$ proportion in synthesis gas II, as compared with synthesis gas I. That the yield in the second stage is actually affected by the $CO:H_2$ ratio, is shown by a comparison of all such balance measurements where differences occur in the composition of the gas in stage II. A summary of such analytical evaluations show that with $CO:H_2$ ratio of

1:1.6	about 105 g/cu meter of useful gas
1:1.7	110
1:1.8	120
1:1.9	a maximum value of 130 g.
1:2.05	shows a decrease to 120 g.

These observations are mentioned only to indicate how far the balance calculations based on gas analysis enabled us to make predictions.

Since the correctness of these predictions depends only upon the suitability of the sampling and the accuracy of the gas analysis - and these requirements are not problems for us - the possibilities of error were no greater than in the customary method of measuring yields.

This paper is followed by 10 pages of general discussion.

Frame 488-506. Development work in the field of iron catalysts.
By Dr. Meyer.

In a series of studies on iron catalysts, a specific aim was the discovery of catalysts which would permit a regulation of the synthesis reaction in the direction of either light or heavy hydrocarbon products. Cobalt catalysts at normal pressure always favor the production of light naphthas, at medium pressure the paraffin wax products predominates.

It is known that increased temperature favors the production of lighter products at the expense of the higher boiling materials. However there is also the possibility that carbon monoxide will be completely broken down, with the resultant formation of elemental carbon.

It was desirable to obtain an iron catalyst in such condition that its hydrogenation efficiency could be regulated to produce light or heavy hydrocarbons at the same reaction temperature. This was affected by a gas pretreatment of a specific catalyst.

Since yields at normal pressure were inferior to those with cobalt catalysts, stress was laid on developing materials for use in medium pressure synthesis. It was found that catalysts with higher iron content (i.e. without carriers) tend to direct the medium pressure reaction toward the formation of paraffinic compounds, while catalysts which include carriers, particularly kieselguhr, lead to the formation of naphthas. Iron catalysts free from carriers, are greatly influenced by alkali content, pretreatment and startup operations.

Catalysts were prepared almost exclusively by precipitation with soda from a solution of iron in nitric or other acid.

Particularly good results were obtained with two catalysts containing copper, and designated as M_1 and M_2. By subjecting these catalysts to thermal pretreatment, it was possible to shift the reaction sharply from the production of light to heavy hydrocarbons. Both catalysts also contained very slight amounts of alkali.

The synthesis gas used, for medium pressure synthesis with iron catalysts, comprised a CO-rich gas of approximately 1.6-1.7 $CO:1H_2$ proportions. Using the M_2 catalyst in small scale tests, it was possible to obtain up to 180g liquid product (including gasol) for each cubic meter of synthesis gas., at a CO conversion of about 75-85% volume. The average yield during a 3-months run without regeneration, corresponded to a CO conversion of 84% liquid product.

Tests were made to determine the effect of increasing the temperature. Raising reaction temperatures from 253 to 295°C did not injure the catalyst. Stabilized gasoline produced in these small scale experiments had an octane number 73 and contained 56% olefins.

A study on the effect of pressure indicated that optimum activity was reached between 10-15 atmospheres. With increasing pressure, the paraffin fraction increased.

A third catalyst, M_3, which contained a small amount of alkali in addition to iron, favored the production of heavier paraffins.

A catalyst was tested which was prepared from "Lautamasse", a by-product of the aluminum industry. This contained, in addition to iron oxide, considerable amounts of aluminum oxide, titanium oxide, and calcium oxide, with smaller amounts of silicic acid, magnesium oxide, sulfates and phosphates. Crude Lautamasse at temperatures of 250-260° showed good activity for medium pressure synthesis. The olefin content of conversion products obtained with it is appreciably greater than in the products obtained with other iron catalysts.

It was found that incorporation of considerable amounts of K_2CO_3 in the catalyst mass led to the formation of oxygen compounds, particularly alcohols.

The entire series of experiments led to the development of iron catalysts which were suitable for various purposes.

Frame 507-510. Increase of paraffin fraction in the products
of existing synthesis plants.
By Dr. Roelen.

Experiments were made with cobalt catalysts, for the purpose of increasing the paraffin fraction in medium pressure synthesis. This result was achieved by the use of concentrated cobalt catalysts in combination with activators such as thorium or manganese.

ITEM 125. KNOCK DETERMINATION OF SYNTHETIC GASOLINE.

Frame 511-548. March 9, 1944.

A series of cooperative tests on synthetic gasoline was made by seven organizations including Brabiag, Hoesch, Krupp and Ruhrchemie. Unfortunately the film is so thin that most of the report is practically illegible.

Evaluating tests were made on: tendency toward peroxide formation, relationship between peroxide number and octane number, comparison of methods for knock evaluation and distribution of detonating effect. A series of tables gives the results of the tests, and 6 sheets of curves reproduce graphically the results obtained at the various testing laboratories.

ITEM 196.

Frame 549. Determining activity of the synthesis catalyst
July 2, 1942.

This is a request for permission to study methods for determining catalyst activity, with the aim of standardizing such a method for general use.

ITEM 127. CALCULATIONS OF RESIDUAL GAS ANALYSIS IN PRESSURE SYNTHESIS

Frame 550-555. Example of the evaluation of a residual
gas analysis in pressure synthesis
March 28, 1940

This report consists in an example of the method of calculations used in evaluating an analysis.

ITEM 128. ALCOHOLS FROM MEDIUM PRESSURE SYNTHESIS.

Frame 556-557. Alcohols from medium pressure synthesis
December 28, 1943

A method is noted for increasing the concentration of alcohols recovered from the products of pressure synthesis, through carefully regulated fractionation.

ITEM 129. LIST OF SECTIONS OF RUHRCHEMIE

Frames 558-559.

ITEM 130. MONTHLY SUMMARIES OF DATA, 1938-1941, FOR ALL LARGE-SCALE GERMAN PLANTS.

Frames 561-606.

These reports are in the form of tables giving the average production, month by month, of the various units. The dates of the tables are: March 1940; November 1939; October 1939; September 1939; July 1939; June 1939; May 1939; April 1939; March 1939; February 1939; October 1938; September 1938; August 1938; July 1938; June 1938; May 1938; January 1938, and a combined summary for 1937.

ITEM 131.

Frame 607. Preparation of mechanically strong synthesis catalyst January 23, 1943.

Directions are given for the preparation of the cobalt-thoria-kieselguhr catalyst, mixed with pretreated silica gel. Varying the proportion of kieselguhr to silica gel results in the formation of a softer or harder catalyst.

ITEM 132.

Frame 608-609. Polymerization of diesel oil fractions. July 1, 1941

A sample of diesel oil was polymerized in two lots with 5% $AlCl_3$ each. The polymerization products were examined. The lubricating oil fraction above 370°C shows not only a high specific gravity but an extremely high viscosity pole height. It cannot be used for a lubricating oil.

Frame 610 gives the identification of Bag 3446 (CIOS Target 30/5.01. Ruhrchemie.

Frame 611-612. Index of documents in Bag 3446.

It may be noted that TOM Reel 45 includes only the first 23 of the documents here listed.

BAG 3446. ITEM 1. LUBRICATING OIL SYNTHESIS RESEARCH REPORTS

Frame 613-614. A brief note dated March 17, 1943, accompanies a sheet of curses which indicate the relationship between viscosity pole height, volatility and flash point of a synthetic oil.

Frame 617-621. Oil synthesis, using a C_7 fraction of active-carbon naphtha dehydrogenated with bromine.

A C_7 hydrogenated fraction from synthesis gasoline was dehydrogenated by means of bromine over pumice, and a normal heptane from I.G. was similarly treated. The olefins obtained were then introduced into the unit for the synthesis of lubricating oils. Previous findings were confirmed that the fraction from the activated charcoal synthesis gasoline gave poorer yields and of inferior quality. This is probably due to the position of the double bond in the carbon chain. Any isomerization during dehydrogenation with halogens seems highly improbable. Experimental results are given in three tables.

Frame 622-644. Experimental results on the olefin balance of the Dubbs cracking units, November 1942 and January 1943.

Frame 645-649. Investigation of the exhaust gas from lubricating oil synthesis operations. January 5, 1942.

Analyses were made on the exhaust gases from the dechlorinating tower, the end gases, and the gases obtained on atmospheric final distillation. The latter gases showed high olefin content. Tables are given which show the results of the analyses.

Frame 650-653. Preliminary treatment of the primary products for lubricating oil synthesis. November 21, 1941.

A method for the pretreatment of feed stocks for lubricating oil synthesis must satisfy two conditions:

1) The hydroxyl number must be reduced to about 1. Normally the OH numbers of the 60-200°C fraction of recycle naphtha are around 25. In other words, a 95-98% removal of alcohols must take place.

2) The process by which this removal is accomplished must be so adjusted that, so far as possible, no shift occurs in the position of the double bond.

Five processes have been developed by which it is possible thus to pretreat naphthas and meet the cited requirements. Of these methods, three are hot and two are cold.

The hot methods are:

~~1) Passing the naphthas, in vapor phase, over clay at ca 250°~~

2) Passing it through an 80% solution of phosphoric acid at 140°

3) Passing through an 80% solution of $ZnCl_2$ at 150°.

The cold methods consist of extraction with:

1) Zinc chloride solution

2) Phosphoric acid.

Some other extraction agents have also been used, and a number of other solid materials, but technical defects were such that they will not be discussed. Detailed instructions are given for the procedure in each of the five cases. In all cases a neutralization of the naphtha by treatment in the vapor phase with soda-lime must precede its introduction into the synthesis unit.

Frame 654-661. Extraction of the contact oil hydrocarbons and their conversion into usable lubricating oil. October 28, 1941

The material designated as "contact oil" which is the actual catalyst in polymerization reactions, is a complex of $AlCl_3$ and olefinic hydrocarbons. This complex is produced in considerable excess during the polymerization of cracked gasoline to produce lubricating oils. Since a considerable amount of hydrocarbons, as well as 30-35% of inorganic material, are present in this oil, some type of reclamation should be practiced.

Extraction with organic solvents is not satisfactory, nor is a decomposition in aqueous phase with caustic soda, sulfuric acid and water.

Two samples of the "contact oil" were studied. The properties of the original complex are given and the properties after treatment for 3 hours with 1% Tonsil and 1% $ZnCl_2$.

A suggestion is made that the hydrocarbon- $AlCl_3$ complex itself be used as a catalyst. Detailed description is given of a series of experiments along these lines. The properties of the resulting products are reported. Frames 660-661 reproduce a tabulation of the results.

Frame 662-667. Estimates on lubricating oil production from the products of an iron catalyst synthesis. August 15, 1941

Primary products from syntheses using iron catalysts are better suited for lubricant manufacture than those from syntheses with cobalt catalysts. Experimental results from two cases are made the basis for cost estimates on the process.

Frame 669-672. Tests on cracked gas scrubbing in the Dubbs unit, March 3-10, 1941.

In order to increase the ethylene content, and remove the C_3 and C_4 hydrocarbons, a scrubbing process for cracked gases is proposed. This operates at 3.5 atmospheres and uses stabilized activated carbon naphtha for a scrubbing liquid. A flow diagram of the process is included.

Frame 673-679. Analyses of cracked products
March 28, 1941

Samples were taken of cracked naphtha, refrigerated naphtha, residual gas and bottoms. These samples were carefully fractionated and broken down into individual compounds. The numeric data of the fractionations are given in a series of table.

Frame 680-683. Study of cracked products from Dubbs unit
March 15, 1941

In order to develop an accurate carbon balance, a study was made on cracked gas and cracked naphtha. The gas was subjected to low temperature distillation and the gasoline to close fractionation. The analytical data are summarized in three tables.

Frame 684. Burning tests with decomposed "contact oil"
April 23, 1941

Decomposed hydrocarbon-$AlCl_3$ complex was tested as a fire hazard. While phosphorus was not capable of igniting it, an electron-thermite torch caused the mass to burn on the surface, while intensified torches kindled the oil more quickly. It is evident that a pool of such material would form a decided fire hazard.

Frame 685-689. Lubricating oil plant
April 8, 1941.

Distillation of the residue from two types of spindle oils from the Lurgi plant are given, along with complete distillation analyses.

Frame 690-691. Results in separation tests at Krupp and Bergedorf
March 24, 1941

Sample separation tests were made by Krupp at Essen and by the Bergedorf Iron Works in Hamburg, using 200 liter samples consisting of a mixture of 2/3 upper layer and 1/3 contact oil. The separation in both cases yielded 3 components: 1) a naphtha-oil mixture (upper layer), 2) contact oil, and 3) a solid asphaltic residue from the contact oil.

~~This residue remained on the separator drum and retarded operations.~~ A definite connection was noted between rotation speed and the amount of asphalt separation. The contact oil flowed from the drum more rapidly at 5500 RPM than at 8000 RPM. It was proposed that two centrifuges be connected in series, the first with a large sludge chamber and slow rotation speed, the second of normal construction, for fine purification.

Frame 692-693. Refining of contact oil
February 10, 1941.

The contact oil consisted of 77.5% hydrocarbons and 22.5% $AlCl_3$. By decomposition with water, 77.5% hydrocarbons were recovered from the oil. Distillation of the oil fraction, disregarding losses, yielded 55.5% hydrocarbons boiling above 360° and 18.9% boiling up to 360°.

The procedure for breaking down the contact oil is described.

Frame 694-695. C_5 content of refrigeration naphtha
and heavy naphtha
December 21, 1940

Naphtha samples from various units were tested for different hydrocarbons:

At 70°C	C_3	C_4	C_5	Resid.
Refrigeration naphtha	13.5%	20.5	20.7	45.3
Heavy naphtha	0.9	2.1	4.1	92.9
At 100°C				
Refrigeration naphtha	9.4	17.9	16.7	56
Heavy naphtha	0.7	1.1	3.0	95.2

Frame 696 Acid content of cracked naphtha
December 9, 1940

Acid numbers of water and naphtha were determined on the contents of Receivers 1 and 3 as follows:

	Water	Naphtha
Receiver 1	1.5-1.9 mgKOH/g	0.7-0.9 mgKOH/g
Receiver 3	1.3-1.8	0.7-0.9

This high acidity resulted in the recommendation to use acid-resistant materials in the condenser tubes.

Frame 697. Flash point of very viscous oils in closed cup
December 6, 1940

Two oils which were tested for flash point with open and closed cup apparatus showed a difference of around 65° in the results of the two methods. The more viscous oil (48°E) was subjected to distillation at 0.4mm pressure until 6% had been removed. The residue showed the following characteristics:

d_{20} 0.871

V_{50} 51.5°E

Flash open cup	339
Flash closed cup	230

Frame 698-699. Preparation of uniform motor oil from 2X oil, 3X oil and synthesis oil.
November 16, 1940

Mixtures of these oils were prepared in an attempt to produce a good motor oil. While the properties of the 2X and 3X oils are noted, no information is given as to their origin.

Frame 700 Chlorine content of the dechlorinated upper layer
November 12, 1940

Two samples of the upper layer, after deacidifying, were examined with regard to chlorine content. It was found that some chlorine was present and could be released as hydrogen chloride gas.

Frame 701. Volatility of motor oil
November 7, 1940

Mixtures of oil stocks were blended with varying percentages of spindle oil in an attempt to produce an all-purpose motor oil which should not evaporate too rapidly.

Frame 702-703. Mixtures of spindle oil and motor oil
October 31, 1940

Spindle oil was mixed with motor oil in the proportion of 1:10. The mixed oil shows an evaporation loss of 10%. This satisfies the requirements.

Frame 704-705. Dechlorination in oil synthesis
October 15, 1940

A very brief description, accompanied by a sketch, of a device for removing chlorine from the lubricating oil installation, in order to reduce corrosion.

Frame 706-708. Manufacture of 150 tons of 5°E. oil
September 14, 1940

The task was assigned to prepare 150 tons of oil with a viscosity of 4°E. The oil would have to be a distillate since the evaporation test could not be too high. During the period from September 7 to 11, crude oil was distilled to a resid of 24°E (flash point 310°C, oil 308, Tank S9) and the distillate oil of 3-4°E (flash point 210°). This distillation did not yield a sufficient amount of oil. Other oils were distilled and the mixtures brought to a uniform viscosity by circulation pumping. The resultant product was designated Oil 3095. This was to be added to regenerator oils, to produce an all-purpose motor oil.

Frame 709. Letter transmitting a report on "Means for producing lubricating oils with viscosity index of 120 from cracked products".
September 12, 1940

Frame 710-715. Measures for the preparation of lubricating oils with an index of 120 from cracked products
September 12, 1940

Lubricating oils with an index of 120 correspond to a pole height of 1.50. According to our experience, such oils, from high boiling cracked products, can be polymerized above 200°C. The cracking stock should have an initial boiling point of about 280°C. The solidifying point of this material is around +28 to +32°C.

Cracking such a product yields the following products:

Cracked naphtha	65.9%
Refrigerant	11.8
Total naphtha	77.7%
Cracked gas	21.8%
Resid.	0.5

The total naphtha is cut into different fractions which are polymerized individually. The results are summarized in an accompanying table. The high-boiling fraction, 220-275°, produces an oil with an index above 120. Through the effect of this fraction, oils with the desired index of 120 can be produced from a cracked naphtha having an initial boiling point above at least 100°. The entire yield of cracked naphtha must be fractionated. If the naphtha is divided into two fractions, one comprising refrigeration naphtha and other products up to 150°, and the other from 150° up, the lower fraction can be polymerized to lubricants with higher viscosity index. The higher boiling fraction comprises the C_8 to C_{15} hydrocarbons. By combining the products, blends can be prepared with a satisfactory index. Two tables of data are given.

Frame 716-722. Dechlorination in oil synthesis - October 12, 1940

Dechlorination in oil synthesis is studied by means of an indirect analytical method, in which the neutralization numbers are determined. A different method was under development in which a determination was made of the hydrochloric acid which could be split out by steam distillation. This is of direct technical interest, since HCl is split out in atmospheric as well as in steam distillation. Dechlorination may cause some difficulties, but there was general agreement that it had accomplished what had been expected. Poor results were obtained when charges from leaky condensers were treated. Moist products are extremely hard to dechlorinate.

Continuous dechlorination was under consideration at Ruhrbenzin. Here, for a period of time sufficient Tonsil-zinc oxide packing would be disposed in a large tower and the upper layer of product, which was to be dechlorinated, would be passed through the tower. It was pointed out that there was danger of poor distribution of liquid, because of the possibility of channeling, agglomeration, etc. The use of metallic zinc in combination with Tonsil was proposed as a dechlorinating agent. A pilot plant of about 100 kg/hr. capacity was proposed, to study a continuous dechlorination process.

Frame 723-732. August 5, 1940

Operating data for a full scale lubricating oil plant are summarized, with reference to guarantees for Japanese licensing. This was a synthetic process for making lubricating oils by polymerizing the products from a cracked naphtha.

ITEM 2. WATER GAS RECIRCULATION - PRODUCT ANALYSIS

Frame 733-735. Product analysis of a synthesis
with water gas circulation
September 17, 1940

This merely gives a product analysis, but no information concerning the conditions of the operation.

ITEM 3. BLACK WAX

Frame 736. Investigation of black wax
March 20, 1940

The wax was subjected to exhaustive extraction with ethanol and with acetone. The residues were tested for benzene solubility and the final resid to acid decomposition. A complete removal of sulfates was obtained from the organic fraction dissolved in benzol.

Frame 737. Studies of black wax.
March 8, 1940

Summary of the results of studies on black wax indicated that from the wax, by treatment with solvents, an insoluble, ash-rich residue can be recovered. This was decomposed with sulfuric acid into the sulfates of cobalt, thorium and magnesium, and an organic fraction which was now soluble in solvents. Work on black wax had to be interrupted.

Frame 738-741. Previous results of studies in the black wax
obtained from operation of the pressure synthesis
furnaces - March 5, 1940

A black wax produced from furnace 204 was subjected to investigation. The wax was deep black and had an odor of amino compounds. The water content was 6.0%, the ash content, 5.5%.

Extraction:

An attempt to extract with benzol in a Soxhlet or Peters extractor was not successful, because the wax swells on contact with the solvent, then rendering the filter impermeable. A suggestion that benzol extraction might be hindered by the water content of the wax led to the proposal for using a water-soluble or water-dissolving material as a solvent. Such solvents are acetone or ethanol.

Black wax can be extracted with both solvents without difficulty, and a white paraffin is recovered; the pigmenting constituents remain in the extraction capsule. Both acetone and ethanol have only slight capacity for paraffin, therefore a complete extraction would be time-consuming.

The assumption that the more favorable behavior of acetone and alcohol was due to their water-solvent capacity, proved to be erroneous.

Solution:

With benzol. Wax was boiled with benzol several times; 400 grams were heated with 2 liters of benzol and refluxed for 2 hours, and the solution was cooled; the residual wax was suctioned off and again treated with benzol. After distilling off the benzol, the amount of paraffin dissolved was determined.

The residue was dried in vacuum at 50°. It was a hard dry powder of dark brown color. The insoluble residue amounted to about 25% by weight of the paraffin - appreciably higher than the ash content.

Extraction with Carbon Tetrachloride:

When black wax is boiled with CCl_4, a result was obtained similar to that found with benzol. By 5 to 6 treatments, the most of the paraffin was brought into solution. The final residue from CCl_4 treatment was of dry powdery consistency and gray in color.

Settling tests:

Black wax dissolved in cold benzol produces a dark opaque solution. On long standing, black flocks begin to settle and the liquid changes from black to dark brown, then light brown and becomes more transparent. When the benzol is distilled off, a white paraffin is left. The black, benzol-insoluble residue, after drying with vacuum, was a dark brown hard powder.

Properties of insoluble residue:

The benzol-insoluble residue, after heating to incandescence, was treated hot with 10% H_2SO_4. Inorganic constituents (cobalt) went into solution; a dark cake remained which melted when heated.

Analysis of 20 g of the residue showed:

organics	11.7g
inorganics	4.4
kieselguhr and loss	3.9
Total	20.0g

The resid contains cobalt, thorium and magnesium.

The cake, purified with Tonsil, was faintly brown in color, practically odorless and had the character of a high-melting paraffin.

Frame 742. Black wax, plant scale.
December 22, 1939

An ultimate analysis of the sample gave:

75.65%	C
13.15	H
4.65	O
1.01	N
5.54	Resid

This indicates considerable nitrogen, which could be noticed from the odor of amines.

ITEM 4. MEDIUM PRESSURE PARAFFINS

Frame 743-744. Medium pressure paraffin samples.
January 12, 1939

Samples of paraffin from the pressure cycling furnace, and from a normal furnace, were submitted for study. The operating data on the furnaces were: Furnace No. 2: 216°, circulation 1:4 water gas,; pressure 7 atmospheres. A collective sample was used.

The products from the run were:

Active carbon naphtha	68.6%
Oil condensate	28.8
Paraffin	2.6

Furnace No. 3: Daily sample Dec. 10-11, 1938. 189-191.5°, synthesis gas, 6 atmospheres, 1580 hours of operation.

Products from the run:

Active carbon (A.-K.) naphtha	18.0%
Oil condensate	43.1
Paraffin	38.9

Since the condensate oil contains small amounts of wax, this must be taken into consideration during mixing.

Furnace No. 4. Daily sample, Jan. 6-7, 1939. Temperature, 192.7°, 924th hour of operation, 5 atmospheres:

Products:		
	Active carbon naphtha	14.4%
	Oil condensate	32.7
	Paraffin	52.9

The entire fraction boiling above 320° is included with the naphtha.

Furnace No. 8. 7-day sample, January 2-3, 1939.

Temperature 199.5°, 5 atmospheres, synthesis gas, 2144th hour of operation.

Operation with reversed flow, from bottom to top.

Active carbon naphtha	33.7%
Oil condensate	34.6
Paraffin	31.7

Frame 745. Soft wax
Nov. 17, 1941

The amount of soft paraffin in the products of medium pressure synthesis at Ruhrbenzin could not be stated. The Hoesch plant produces a soft paraffin content boiling between 320 and 450°C of about 16.8% of the total product.

In water gas circulation, a soft wax fraction boiling 320-460° amounted to 17.5%.

Frame 746-747. Paraffin production with water gas cycling
November 3, 1941

In a water gas recycling plant, using a cobalt mixed catalyst, 24.0% of paraffin was produced - 6.5% hard wax and 17.5% soft wax (boiling range 320-460°).

Figures are given for Ruhrbenzin and Rheinpreussen results.

ITEM 5. PROGRAM FOR MEDIUM PRESSURE RESEARCH - May 27, 1942.

Frame 748-750.

After a list of projects is given, the statement is made that the purposes of all pilot plant synthesis experiments are to increase yields and recover the most valuable primary products, these are the olefins.

Frame 751-753. Status of experimental program as of January 20, 1942.

The tests currently running were:

1. A life test of more than 4 months, with an iron catalyst, and using water gas makeup.

2. Study of the effect of H_2/CO ratio in the synthesis gas on medium pressure syntheses with direct passage over cobalt catalyst.

Certain tests which are scheduled for early study include a 6-months run in a double tube furnace, cobalt catalysts, water gas recycle; the use of residual gas from water gas recycle as the second stage gas over cobalt, and experiments on shutdown, and iron catalyst synthesis.

Frame 754-755. Experimental program of DVA, July 21, 1941. Status of tests.

Frames 766-767. Experimental program of DVA, July 21, 1941. Status of tests.

Frames 758-759. Research program of medium pressure synthesis plant, June 20, 1941. Report of status of work.

Frames 760-761 are duplicates of 758-759.

ITEM 6. MEDIUM PRESSURE SYNTHESIS.

Frame 762. Letter dated August 8, 1939, suggesting that a eutectic mixture of diphenyl and diphenyl oxide might be used as heat transfer agent in iron catalyst experiments.

Frame 763. Olefin synthesis at normal pressure in direct passage with gases rich in inerts. December 14, 1942.

A letter transmitting data obtained in normal pressure synthesis with a vertical finned tube furnace. Frames 764-765 give the numeric results and a schematic diagram.

Frame 766-767. Influence of the content of inerts and CO/H_2 upon synthesis. November 22, 1940

The following tests are proposed: Variation of the CO/H_2 ratio in the fresh gas, the unit to be operated first with Ruhrbenzin residual gas, then after 5 days converted to operation with synthesis gas, mixed gas and water gas. The shift in the CO/H_2 content from 1.26 to 1.55 and 2.0 can be recognized by the change in olefin formation in the liquid products, in the gasification and other synthesis characteristics.

In a second series of tests it is proposed to vary the amount of inerts in the fresh gas.

Frame 768. Gasification of catalyst in medium pressure synthesis April 17, 1939

A table shown the results with several mixed catalysts, largely magnesiathoria complexes.

Frame 769-770. Carbon monoxide balance for medium pressure synthesis January 31, 1939

A letter transmitting data on the results from 3 types of operation: direct passage with 75% CO conversion; recycling, also with 75% CO conversion, and higher temperature recycling with 94% CO conversion.

Frame 771-773. Furnaces for olefin synthesis December 30, 1941

The charge of the unit for olefin synthesis was selected under the assumption that the same converter capacity would be achieved as that given by Ruhrbenzin, with a conversion of 92-95%. The most important task was to produce a specified amount and type of olefins. Two tests, extending over several months, were made, one with 1000 and the other with 800 cubic meters of synthesis gas. It was found that the smaller load was preferable, since it produced a larger yield with higher olefin content.

It is also stated that the paraffin content can scarcely be increased, if the greatest capacity of the unit is to be utilized.

Frame 774. Neutralization numbers of products from the olefin synthesis, water gas recycled 1:3 at pressures of 7 atmospheres, using cobalt mixed catalyst. June 6, 1941.

Neutralization numbers of the products from water gas recycle synthesis were determined as follows:

A.K. naphtha	0.02-0.10 mg KOH/g
Oil condensate	1.2 -1.7
Paraffin scale	1.0
Water of reaction	1.2 -1.4
A.K. water	0.1 -0.15

The product distribution was as follows:

A.K. naphtha	33 kg
Oil condensate	50
Paraffin scale	17
Water of reaction	165
A.K. water	96

A neutralization number of 1.18 mg KOH/g for the entire liquid reaction product was obtained.

ITEM 7. WAX FROM IRON CATALYST SYNTHESIS.

Frame 775-776. Paraffin from iron synthesis
January 19, 1942

The statement has been made that the initially high paraffin content decreases more and more as the catalyst ages, independent of conversion and temperature. This is not affected by stopping the operation. The curves of paraffin content show a constant downward direction with increasing age of catalyst.

Frame 777-778. Attempts to recover crude wax with iron catalysts.
November 18, 1940

Iron catalysts, introduced for the purpose of recovering crude wax to be used in the synthesis of fatty acids, produced various results.

The largest amount of crude paraffin boiling above 320°C was obtained with the last introduced catalyst in Furnace 11 - 100 Fe, 10 Ca, 5 Cu, 100 kieselguhr, precipitated with KOH. In 67 days' operation, about 44% (weight) of material boiling above 320° was produced. Of this, 32% comprised soft wax and 68% hard wax.

Therefore approximately 14% of the total product would be directly applicable to fatty acid synthesis, while 30% could be made available by cracking.

ITEM 8. COBALT CATALYST RECIRCULATION

Frame 780-781. Water gas recycle
May 15, 1939

A sample of naphtha, produced with dilute cobalt catalyst was analyzed. The conditions were, 20 atmospheres pressure and 237°C temperature, recycled water gas feed. Analytical data are given in Frame 781.

Frame 782. Water gas naphtha, Lurgi,
May 17, 1939

The octane number was compared to that of untreated naphtha, to show that higher reaction temperatures alone caused no change in the properties of the olefins. Undoubtedly the octane number would be altered by treatment with bleaching earths.

Frame 783. Recycle experiments with synthesis gas
November 24, 1938

Using a Co-ThO_2 catalyst, at 200°C temperature, charging 1.10 cu meters of synthesis gas per kg CO/hour, and recycle of 1: 2.2, a 95%

conversion of the carbon monoxide charged was achieved, and a yield of 149.0 g liquid product for each cubic meter of ideal gas.

The product had the following properties:

Initial boiling point		30°C
up to	100°C	27.4%
	120	34.4
	140	42.2
	160	47.9
	200	58.8
	320	87.6
	360	93.4

The fraction up to 140°C contained 37.0% (volume) olefins. The oil fraction, 200-320°C contained 15% olefin; the octane number of the gasoline fraction (up to 200°C) was 42.0, and after chemical treatment, 50.0. The fraction up to 175°C had a direct octane number of 60.

Frame 784. Comparison of gasoline production by pressure synthesis, using the two-stage method or the recycle method. October 18, 1938

A comment on a report states that an error has been made in calculating the costs for the two-stage process.

Frame 785-787. Excerpt from report: Comparison of gasoline from 2-stage and recycle process. October 19, 1938

The material balance is given for a plant to utilize 41700 cubic meters hourly. Costs are given on Frame 786, and a series of curves on 787.

ITEM 9. IRON CATALYST SYNTHESIS.

Frame 788. Production and composition of Gasol with iron catalyst May 29, 1943

In syntheses using iron catalysts, and operating at around 250°C., with an operating time of 4 months, the gasol forms about 12% of the total product.

~~Its composition is: (in weight percent)~~

Propylene	27%
Propane	27
Butylene	31
Butane	15

Experiments with low temperature iron catalysts are not sufficiently advanced to allow the drawing of general conclusions.

Frame 789-790. Iron catalysts
May 20, 1942

A complaint is noted that iron catalyst No. 1552 had not fulfilled the desired performance in one of the units at DVA. Part of the reason for this lies in the type of furnace. It is probable that improvements in furnace design and operation should be made before making further attempts at catalyst improvement.

An iron catalyst with lower copper content has been studied. Decreasing the amount of copper quite regularly causes a diminution of the paraffin fraction. Other proposed catalyst components, such as silver and iron, have not proved satisfactory.

Frame 791. Iron catalysts for DVA.
April 25, 1942.

The request for a new supply of iron catalyst to be used in the Mannesmann furnace is not considered to be justified. Development of wax producing catalysts has largely been discontinued because of the greater need for catalysts to favor motor fuel production.

Frame 792. Iron catalysts
April 14, 1942

The following results have been obtained in the Mannesmann furnace with iron catalyst F 1552:

Yield, including gasol	Guaranteed	Obtained
a) at 72% conversion	-	115g liquid
		12g gasol
		127
b) at 90% conversion		
Total yield	140 g	150g
Paraffin	63	64.4

The guaranteed yields have been met and exceeded easily.

Frame 793. Yields obtainable in iron synthesis
December 4, 1941

The commercial units with two-stage operation produced a minimum yield of 145.0g with conversion of $CO + H_2$ in both stages equal to 90-92%.

Water gas recycle process in Unit 11, over iron catalysts in 124 days showed a conversion of 75%.

Frame 794. Guaranteed yield.
June 27, 1941

The possible performance which might be guaranteed under different methods of procedure are given. The methods include use of iron catalyst and medium pressure, and use of cobalt catalyst at normal pressure.

Frame 796-800. Character of products from synthesis with water gas over iron catalysts (Furnace 11, 7th run)
November 20, 1940.

A 72-day run gave the following results:

1) Olefin content (P_2O_5-H_2SO_4 soluble)

Gasol	70%
Naphtha -200C	78
Oil, 200-320C	68

2) Acid content:

Neutralization number	A.K. naphtha	0.05 mgKOH/g
	Oil condensate	6.0
	Reaction water	11.0
in naphtha distillate up to 200°C		5.7
oil distillate 200-320°C		0.9

3) Water-soluble products

20g/liter water of reaction = 2.12g/cubic meter water gas.

The gasol, with its high olefin content of around 70%, is particularly suitable for the production of polymer gasoline. Specific figures and tables are given.

Frame 801-803. Composition of products from the test with recycling water gas over a precipitated iron catalyst.
September 17, 1940

All products from Run 7, furnace 11, in the period August 29 to September 10, 1940, were collected and given, partly to one group for inspection and partly sent to other groups for work in the Oxo synthesis.

The operating conditions were:

Charge	1.02 cu meters water gas/ normal value
Gas pressure	19-20 atmospheres
Circulation	1 ◇ 2.7
Temperature	242° average
Contraction	55%
$CO + H_2$ conversion	77.5%
$CO + H_2$ degree of liquefaction,	56.2%
CO conversion	80.5%

The yield of liquid products was 114 g/cu meter gas. A complete distillation analysis is given, as well as other properties such as aniline point, specific gravity, Reid vapor pressure, octane number, iodine number and refractive index.

Frame 804-805. Results of tests with iron catalysts
September 3, 1940

Frame 806. Introduction of iron catalyst from the Research Laboratory of DVA
March 18, 1940

An iron catalyst was prepared which contained 20% kieselguhr, and was supplied in the form of granules. The individual conditions of manufacture must be given further study and reported later.

Frame 807. Mulheim iron catalyst
February 14, 1940

A note from an unpublished manuscript states that Mulheim has been assigned the task of developing an iron catalyst which should produce the highest possible yields from synthesis gas (30% CO, 60% H_2, remainder inerts), and have satisfactory catalyst life.

Certain points of view seem valid and significant: 1) the use of precipitation catalysts; 2) the importance of alkalization and residual alkali content; 3) Mulheim catalyst operated without pressure and produced 50 g liquid/cu. meter mixed gas; 4) starting the catalyst with mixed gas and regenerating by oxidation after a preliminary extraction.

Frame 808. Iron catalyst. January 5, 1940

Frame 809-810. Test with iron catalyst of the Research Laboratory
January 11, 1940

Because of lack or equipment for operating at 20 atmospheres, it was necessary to make tests at pressures of 8-9 atmospheres. Mention is made of the units available and the adjustments needed for use in these tests.

ITEM 10. LURGI IRON CATALYST

Frame 811-812. Lurgi catalysts.
Dec. 8, 1939

Attempts to prepare iron catalysts on a large scale, according to the specifications given by Lurgi were not satisfactory. The catalyst proved to be difficult to filter and wash, and when it was distributed over a large filter surface, the washed cake had a gummy quality which made it hard to shape.

Frame 813-814. Lurgi iron catalysts
November 3, 1939

Work at Ruhrbenzin with the iron catalyst, prepared according to Lurgi instructions, did not produce the yields which Lurgi claimed. Later Lurgi confirmed the poor results obtained when using the same catalyst, but suggested that the presence of small amounts of nickel in the catalyst might be causing the trouble. However no nickel could be detected in the catalyst.

Lurgi then agreed to furnish samples of their own catalyst for further testing.

A dilute cobalt catalyst manufactured for Hoesch was not fulfilling expectations. However this shipment had been hastily prepared and was later stored in paper sacks, so it had probably deteriorated considerably.

Frame 815. Iron catalyst.
October 26, 1939

A letter from Dr. Herbert (of Lurgi) stated that the catalyst to be furnished Ruhrbenzin could not be sent for some time, and therefore suggested postponement of further tests.

Frame 816. Catalysts.
Oct. 21, 1939

A memorandum concerns a telephone conversation in which a proposal was made to alter the operation of recycle process with Lurgi catalyst by decreasing the recycle to 1:1.5 in order to reduce hydrogen consumption.

Frame 817. Table showing the performance of iron catalyst in Stage I, October 19, 1939.

Frame 818-819. Previous experimental results with Lurgi iron catalyst
October 14, 1939

A sample of iron catalyst, prepared by the Research Laboratory according to Lurgi specifications (100 Fe, 5 Cu, 9Al_2O_3, 120 kieselguhr) was delivered to Lurgi. This catalyst was more active than the sample prepared by Lurgi itself. It operated at about 8° lower temperature but caused higher gasification. It did not, however, cause such a high degree of liquefaction. This may be due to the use of a different kieselguhr or other raw materials, or to individual difference in the method of catalyst precipitation.

Additional tests were to be made by both Lurgi and Ruhrbenzin in an attempt to obtain concordant results.

Frame 820-821. Experiments with iron catalysts.
October 7, 1939

The results of a test with an iron catalyst are given:

Operating conditions:

Catalyst chamber diameter,	10 meters
Depth of bed	3 "
Pressure	20 atmospheres
Temperature	235°C
Recycle	1:2.5

Gas analysis	Feed gas	Resid Gas
CO_2	0	15.8
C_nH_m	0	0.2
O_2	0.3	0.3
CO	39.0	24.0
H_2	50.5	34.5
CH_4	0	2.0
N_2	10.2	22.3
C-number	-	1.10
CO + H_2 conversion	70 %	

Composition of products:

Naphtha	-200°C	31%
Oil	200-320°C	25%
Paraffin		44%

The paraffin is pure white, the oil and naphthas are colorless.

Frame 822. Gasoline synthesis
October 2, 1939

A letter from Dr. Herbert of Lurgi, transmitting a letter to Ruhrchemie concerning iron catalysts.

Frame 823. Iron catalyst
October 2, 1939

The iron catalyst sent to Lurgi by Ruhrchemie had practically the same activity as the catalyst prepared by Lurgi, but caused higher methane formation.

Frame 824-825. Lurgi experimental program
July 10, 1939

A proposed program for cooperation between Dr. Bahr and Dr. Herbert is given. This would include the preparation of a synthesis gas with a $CO:H_2$ ratio of 1.8:1 in unit 3. The arrangement of compressors and catalyst chambers should produce a pressure of 20 to 25 atmospheres in the catalyst chamber. A water wash of the gas, either before its introduction into unit 3, or of the residual gas from this unit before its release.

The finned unit (Lamellenofen) should subsequently be connected into the recycle operation.

Frame 826. Lurgi iron catalyst
August 10, 1939

A sample of reduced iron catalyst was furnished by Lurgi to Ruhrchemie. This catalyst was to be used with a gas mixture of 60% CO and 31% H_2, the remainder being N_2 and CO_2. The pressure was 20 atmospheres, initial temperature 235°C, charge 9.1 liters/hour for 100cc of catalyst. Within 2 days the temperature to be increased until a conversion of 75% is reached. Operating temperature is then 245-250°, the yield about 130-135g/cu meter of inert-free feed gas.

Frame 827-828. Results of tests with Lurgi iron catalyst
March 4, 1939

Samples of a Lurgi catalyst were tested in the laboratory of Ruhrchemie. The results which were reported were not favorable, and did not agree with those obtained in Frankfort. It was agreed that Lurgi should be asked to furnish another sample, this time in the reduced state.

Frame 829-830. Preparation of an iron catalyst - no date.

There is required a solution consisting of

240 g $Fe(NO_3)_3$ x $9H_2O$
166 g $Al(NO_3)_3$ x $9H_2O$
32 g $Cu(NO_3)_2$ x $3H_2O$

dissolved in water and made up to 1 liter involume.

224 caustic potash dissolved in water and made up to 1 liter.
40 g kieselguhr

1 film colorimeter
1 nutsch (suction) filter of 30 cm diameter, with a linen filter cloth
1 iron pot of 4-5 liters capacity
1 enamel pot of 2 liters capacity

Procedure:

One liter each of the nitrate solution and the caustic are heated to boiling. The nitrate solution, except for a remainder of 20cc, is poured into the boiling solution of caustic. The pH is determined as quickly as possible by spot tests on an indicator film. Then nitrate solution is added until a pH value of 9.2 is reached. Then into the catalyst slurry, 40 g of kieselguhr are stirred and the entire mass is dumped into the nutsch which has been preheated with steam. Weak suction is applied for half a minute, then strong suction until the liquid has almost disappeared, so that cracks appear in the filter cake as a result of further suction. 800 cc of boiling water are then added to the nutsch, the precipitate is thoroughly kneaded on the nutsch with this water and is again washed with 800 cc of boiling water.

The filter cake is then sharply sucked dry, passed through an extrusion press at 110° and dried to surface dryness. Then at 250 and in a thin layer, it is reduced with hydrogen, using 2 cu. meters of hydrogen per hour per 100 cc of catalyst. The reduction value of the finished catalyst should amount to 2.5% of raw theoretically reducible iron. An amount of 5% should not be exceeded. Catalysts having reduction values of over 20% are practically inactive.

According to the above directions, from the given amount of chemicals, approximately 200cc = 120 g of green catalyst was obtained. The iron content was 27%.

Frame 831-837. Operating data of the I.G. Process

Frame 838. Obtaining a gas rich in carbon monoxide for the feed gas in the Lurgi tests with iron catalyst. January 27, 1939

The use of an Otto generator was proposed in the production of a feed gas having a $CO:H_2$ ratio of 2:1 such as is required for pressure synthesis with iron catalysts. The details of operation make this too expensive to be considered. By mixing water gas and carbon monoxide, the desired CO-rich feed gas can be produced.

Frame 839. Procedure with Lurgi iron catalyst No. 2
January 20, 1939

Operation should be as follows: Feed gas, $CO:H_2$ ratio 2:1, a gas with 60% CO, 30% H_2 and 10% nitrogen is used. Experimental pressure of 10 atmospheres, or better, 20 atmospheres. The catalyst is charged by volume, and used for single pass operation. As initial temperature, 220°C was chosen; temperature can then be raised rather quickly to 240°C. It is increased until 75% conversion of the carbon monoxide is achieved. Operating in this manner, Dr. Herbert obtains a yield of 110-120 g liquid product for each cubic meter of inert-free gas.

ITEM 11. IRON CATALYSTS MISCELLANEOUS

Frame 841-850. Iron catalysts, report of conference
May 8, 1943

Representatives of several organizations discussed possible small-scale and pilot plant tests on catalysts which were intended to replace the cobalt catalysts in some of the syntheses.

Frame 851-852. Iron catalyst synthesis
January 18, 1943

In applying an iron catalyst in the operation of pressure units, the following points may be noted:

1. Cooling in the heat exchangers of the furnaces, by means of low pressure steam cannot be considered, since tremendous quantities would be required, and steam distribution in furnaces of these dimensions would encounter difficulties.

2. The same objections noted under 1 are also true for the use of air. Moreover the difference in temperature between catalyst and heat transfer medium might become too great even for iron catalysts.

3. The proposal to fill the pressure units with a nitrate melt, and by injecting air or inert gases to remove the resulting heat, with simultaneous vigorous agitation, requires a consumption of energy which seems unjustifiable.

4. Apparently the only solution remaining is the possibility of recirculating large amounts of liquid, either nitrate-nitrite melts or oil, to carry away the heat of reaction.

Frame 853. Iron catalyst manufacture at Rheinpreussen.
January 18, 1943

Apparently the synthesis with iron catalysts at Rheinpreussen was a liquid phase operation. The application of this method to low pressure and medium pressure synthesis seems impracticable.

Frame 854-855. Iron catalyst synthesis.
January 12, 1943

The advantages claimed for catalysts developed by Rheinpreussen are questioned, and their defects are pointed out. The Ruhrchemie catalysts were developed to operate under conditions where temperature was not the most important factor.

Frame 856. Iron catalysts
Jan. 11, 1943

It was stated that Rheinpreussen has succeeded in developing an iron catalyst which would operate at practically the same temperature as the cobalt catalysts, i.e. temperatures between 200 and 220°C.

Frame 857-860. Cooling liquid for synthesis units using iron catalysts.
March 31, 1942

In order to learn the extent of possible corrosion caused by the use of a salt bath for a cooling medium, tests were made in iron tubes. The salt melt consisted of 7% $NaNO_3$. 40% $NaNO_2$, and 53% KNO_3. This mixture was introduced into three different tubes, whose inner surfaces had been polished. To the salt mixes was added 1, 2 and 4% water, the tubes were sealed and exposed for 1100 hours to temperatures of 270-280°. It was found that under the described experimental conditions, the amount of iron taken up by the salt was exceedingly slight, and practically without significance for corrosion.

Frame 861. Inspection of catalyst chamber for iron catalyst synthesis

A report on the condition of equipment which had not yet been placed in operation.

Frame 862-865. Variation of octane number of iron catalyst gasoline with end boiling points
January 5, 1942

To ascertain the relationship between octane number and boiling points, the gasoline from Unit 14 (Ruhrchemie iron catalyst unit) was fractionated. As might be expected, the octane numbers rose appreciably with decreasing boiling point. However a comparison with the corresponding curves for cobalt gasoline showed that the rise is practically parallel with that of other curves. An octane number of 63 was reached with index 96, which corresponds to an end point of 165-170°. There are three sheets of summarized data.

Frame 866-867. Iron catalyst furnaces.
January 2, 1942.

These are practically illegible.

Frame 868. Iron catalyst furnace
January 2, 1942

This too is almost illegible, but seems to be a report on the condition of the units.

Frame 869-871. Use of domed unit for iron catalyst synthesis
December 22, 1941

The use of a piece of equipment for iron catalyst synthesis is suggested. This would be operated as a waste heat boiler. A sketch of the proposed scheme is added.

Frame 872. Construction of a large scale experimental plant for carrying out iron catalyst synthesis
February 18, 1941

Interest in iron catalyst synthesis has increased to the point where it is necessary to have an experimental unit which corresponds to a technical installation. Details of furnace construction and operation could then be studied. The unit should be operated on the 2-stage plan, removing CO_2 between the two stages.

Frame 874-877. Iron catalyst synthesis
February 15, 1941

Estimates are given for the cost of constructing vertical and horizontal type units. The vertical type is said to cost M6700 per cubic meter of converter space. Horizontal units with fin cooling equipment would cost around M4900 per cubic meter capacity.

Frame 878. Oil from naphtha produced on iron catalyst under pressure.
February 4, 1941

~~A sample of 500cc of lubricating oil was produced as follows:~~

1. Pretreatment of naphtha:

The 70-180°C fraction of a naphtha was used as starting material, it had an extremely high hydroxyl number of 57, which necessitated intensive pretreating. It was stirred with 10% PCl_5, distilled off from the chloride and refluxed for 2 hours at 80-90° with 5% soda-lime to remove saponifiable constituents. The naphtha now had the following values:

OH number	5
neutralization number	0.02
saponification number	2.96

2. Oil synthesis:

Conditions: stirred at 95°C for 12 hours with 5% $AlCl_3$, Initial oil 11.8% fluid.

Dechlorination with "Tonsil" + 2% ZnO for 2 hours at 180°, atmospheric distillation up to 200°C.

Olefins in the residual naphtha		8% (volume)
Vacuum distillation to 150°		3.7% (weight)
Vacuum distillation to 150-200°		4.2 "
Residuum	200°	45.6 "

Frame 879-881. Iron catalyst synthesis
December 12, 1940

The data are given on one run in Unit 11, using water gas, recycled, and an iron catalyst, composed of 100 Fe, 10 Ca, 5 Cu and 100 kieselguhr precipitated with KOH.

The life of the iron catalyst is shorter than that of a cobalt catalyst, however an effective life of about four months can be expected, according to the activity curve from a 70-day test.

The temperature range should be between 235-260°C (30-50 atmospheres steam pressure). Gas pressure around 20 atmospheres. With improved catalysts it may be possible to decrease this. The recycle makeup should be 1 + 3 in order to maintain the correct $CO:H_2$ ratio.

Frame 882. Synthesis with iron catalyst
October 24, 1940

This frame is scarcely legible.

Frame 883 is a letter dated September 11, 1940, transmitting a report which summarizes the synthesis work with iron catalysts.

Frame 884-889. General observations on tests made up to the present with iron catalysts.
September 11, 1940

In the pressure test installations, six experiments were made with iron catalysts of varying composition and produced by different methods. Certain regularities in behavior led to the suggestion that some general conclusions might be drawn.

The following points are considered:

1. Comparison with previous tests
2. Pre-reduction of the catalyst
3. Kieselguhr content and recycling
4. Composition and olefin content of products.

A table (frame 889) gives comparisons with previous results.

Two catalysts were charged in the unreduced state; no definite conclusions could be drawn from the results.

With regard to kieselguhr and recycling, it was found that increased kieselguhr content as well as increased recycle resulted in a higher consumption ratio. This is particularly important when water gas is processed.

It was found that increase in circulation in all cases - as has been disclosed in water gas synthesis using cobalt catalysts - was always accompanied by an increase in the olefin content. Fractions from iron catalyst synthesis which had formerly designated as olefins were found actually to consist in part of oxygen-containing products.

ITEM 12. TEST COMPARISON OF TWO OVENS.

Frame 890. Experimental results on two furnaces of
different construction
March 8, 1941

Tests were made under like conditions, with water gas recycle 1 ÷ 3. It is shown that a greater heat conducting surface in the furnace has a most favorable effect on the synthesis.

Frame 891-893. Comparison of the 14mm tube furnace (11) with a
normal MD-Mannesmann double tube furnace (10)
March 6, 1941

The 8th run on furnace 11 was made with a normal cobalt mixed catalyst. It was the purpose of the experiment to determine whether furnace 11 was equal in its heat-conductive capacity and therefore in its production capacity, to the normal synthesis furnace.

Furnace 11 contains 267 tubes of 14mm diameter. With a length therefore of 3080mm, there is a furnace volume of 127 liters. Thus for each liter of contact space, there is a cooling surface of 0.286 sq. meters.

Furnace 10 contains at present 27 normal double tubes, in which the inner diameter of the outer tube is 44 mm and the outer diameter of the inner tube is 24 mm. For the length of 4000mm, the furnace volume is 370 liters. Accordingly 2.11 sq. meters of cooling surface is available for each liter of contact space.

The furnaces were operated under conditions as near identical as possible. It was recognized, after 12 days' operation of furnace 10, and 31 days of furnace 11, that furnace 11 was essentially better. The practical degree of liquefaction was so much better that, in spite of a conversion about 3% lower, a higher yield was obtained in furnace 11. All results showed that Unit 11 was not only equal but superior to the normal synthesis furnace in its heat conductivity.

ITEM 13. REFINING OF IRON PARAFFIN.

Frame 894. Iron paraffin
August 27, 1942

Tests were made on the refining of a hard paraffin wax, which had been recovered from furnace 14a of DVA in the period from January to June 1942. This furnace had been operated with water gas recycled over a paraffin-forming iron catalyst. The amount of paraffin formed at first amounted to over 40%, but toward the end of the period it dropped about 5%. Two mixtures were made for testing, designated as Sample I and Sample II. Both samples were yellowish brown, Sample I somewhat darker, Sample II with a cast toward the reddish. Sample I was very difficult to refine; only by treating with 25% Tonsil + carbon, in the proportion of 90:10 could a somewhat brighter color tone be reached. Sample II, on the other hand, was easily refined; with 10% Tonsil & carbon an entirely white paraffin was obtained.

In former paraffin tests with furnace paraffin from cobalt synthesis, a preliminary treatment with H_2SO_4 had proved desirable. This was now tested with iron paraffin; the paraffin was stirred with 50% sulfuric acid for 1/2 hour at 100°. The paraffin was then washed with water and dried. The sulfuric acid treatment, which caused a loss of 1.5-2%, produced scarcely any change in the color of the wax. However so many disturbing elements were removed, that subsequent treating with 10% Tonsil + carbon produced the same result that had been obtained on the untreated wax with 25% Tonsil + carbon. The second sample, which had been refined easily without pretreatment, was also refined with H_2SO_4. No improvement in refining quality could be accomplished.

Frame 895. Paraffin production in iron catalyst synthesis
November 4, 1942

The 9th run of furnace 11 continued from February 22 to June 30 under normal operating conditions, with water gas recycle of about 1 + 2.5-3. The following product distribution resulted:

Naphtha	42% (weight`
Diesel oil	20
Soft paraffin (27°)	14
Plate paraffin (50/52)	4
Hard paraffin (above 85)	20.

Frame 896-897. Refining paraffin from iron catalyst synthesis
July 30, 1941

The total amount of paraffin is dependent to a great degree upon the age of the catalyst; paraffin above 320° decreases from 68% at 227 hours operation to 25% at 289 hours. If the average is calculated over the operating period, the following yields are obtained:

Total paraffin, above 320°C	41.2%
paraffin 320-460	17.9
Plate paraffin	3.9
cold press oil	14.0
hard paraffin (above 460)	23.3

With regard to wax properties, the hardening point of the total wax and that of hard paraffin drops slowly, for total wax from 90 to 70° and for hard paraffin from 93 to 83°. Corresponding to the decreases in hardening point, the material grows softer and the penetration number increases.

Up to the present time, a completely satisfactory product has been obtained only by way of hydrogenation where the hydrogenation was effected with cobalt catalyst after once refining with 1% Tonsil; the operating conditions were, 200° temperature, 100 atmospheres nitrogen-hydrogen during 4 hours operation. Attempts were to be made to see whether it might be possible to shorten the reaction time by using nickel catalysts.

Frame 898-902. Paraffin synthesis with iron catalyst
March 3, 1941

Catalyst:

For the production of paraffin, the best catalyst has proved to be one having the following compositon:

100 Fe, 5 Cu, 10 CaO, 150 kieselguhr.

Increasing the kieselguhr from 100 to 150° introduces a three-fold improvement in the catalyst:

1. Reproducibility in production is facilitated by better washing.
2. Heat distribution during the synthesis is improved, resulting in less gasification and higher yield.
3. Cost of catalyst undergoes a lowering, which corresponds to the higher proportion of kieselguhr.

The catalyst is prepared by precipitating the hot solution with 9,7% KOH upon kieselguhr which has just previously been rendered alkaline.

Cleaning the filter press requires about 30 minutes, and is thus somewhat slower than washing out cobalt catalyst which requires around 25 minutes. The longer time is probably due to the structural difference between hydroxide and carbonate precipitates. Increasing the cleaning time beyond the stated period brings no notable improvement in the scrubbing effect, and shortening the time seems undesirable for safety reasons.

Reproducibility of the catalyst depends strictly upon the accurate maintenance of favorable precipitation and washing conditions. Deviations cause an immediate decrease in yield, change in the composition of the products, shifts in the $CO:H_2$ ratio, etc.

Molding or shaping of the catalyst has been exclusively in the form of filiform granules, 2mm in diameter.

Reduction of the catalyst occurs on a small scale at 300°C in a half-hour's time. Reduction in large scale must follow closely that of laboratory operation if complete catalyst activity is to be obtained. Further tests on large scale reduction seem desirable.

The reduced catalyst has an excellent grain hardness. Confirmatory tests with the catalyst manufacturer have shown that the drum attrition of the catalyst is 2-4% as compared with 15-20% for the best cobalt catalysts. This property of grain hardness insures a smooth and uniform charging into the furnace.

The weight of one liter of the iron catalyst is around 400 g. the iron amounts to 125-130g Fe/liter.

Synthesis:

Paraffin synthesis with iron catalyst is preferably effected with water gas at a pressure of 10 to 20 atmospheres; usually 15 atmospheres was used. Operating temperature was between 225 and 250°C. Introduction of gas into the recycle seems to increase the catalyst life. The normal charge operates with a recycle of 1 : 2 or 1 : 3.

There is also the possibility of operating with direct single pass procedure, since the principal objection –– namely the maintenance of proper $CO:H_2$ ratio in the end gas for the second stage –– is eliminated with this catalyst. The following example indicates this:

	Water gas	End Gas	
		After recycle 1 : 2	After once thru
CO_2	6.3	26.1	29.2
CnHm	0	0.5	0.3
O_2	0	0.1	0.1
CO	38.9	27.1	23.7
H_2	48.8	32.6	31.7
CH_4	0.5	1.8	2.0
N_2	5.8	11.8	13.0
Ratio $CO:H_2$	1:1.26	1:120	1:1.34

This method of treating the gas, which is regulated by catalyst manufacture, completely obviates the necessity for adding another gas which may be richer in CO, and makes possible the operation with water gas, even when variations occur in the CO:H_2 ratio during gas production.

Catalyst life can be considered equal to that of the cobalt catalyst, that is, around 4 months. Removal of spent catalyst, after careful deparaffination, can be effected without difficulty. The catalyst after dewaxing was still granular and hard, and flowed smoothly so that a subsequent cleaning of the individual tubes was practically unnecessary.

Yield and Products:

With the above described catalyst the following excellent yields were obtained, from a one-stage recycle operation:

CO conversion	67%
H_2 conversion	68%
Consumption ratio CO:H_2 =	1:1.29
Gasification (CH_4)	2.5%
Yield, liquid products	123g
Yield, "gasol" products	6g

On further working up in a second stage, up to 90% conversion of CO is achieved with a yield of about 170g including gasol.

Boiling range of the products:

Naphtha (up to 200°C)	15%
Oil 200-320°C	15%
Paraffin 320°C	70% (up to 75%,

The average composition of the paraffin is 1 part soft wax and 3 parts hard; its color is pure white. In the course of several weeks, the paraffin fraction of the products undergoes a gradual decrease to 65-60%. During 2-1/2 months operation, an average of 60% paraffin could be produced.

The naphtha and oil are water-white; tests for olefin show:

Naphtha	to 200°C	72% SPL
Oil	200-320°C	65% SPL

On the basis of iodine-thiocyanate number, the true olefin content is:

Naphtha	57%
Oil	47%.

It may be mentioned that it is possible to convert the paraffin producing catalyst into one which forms gasoline predominantly by a simple change in the precipitation agent, e.g. from KOH to Na_2CO_3.

ITEM 14. LUBRICATING OILS, MOTOR TESTS.

Frame 903-909. Motor oil tests on the Opel 1.3 liter test engine May 8, 1939

Fifteen life tests were made using various motor oils as follows: a residual oil from the synthesis process, without further treatment; the same oil treated with granosil; a residual oil treated on semi-technical scale with $AlCl_3$; a mixture of 80 parts residue oil and 20 parts distillate; $AlCl_3$ oil from large scale operation, recovered from the cold press oil and treated with 1.5% $AlCl_3$; a mixture of two "Gargoyle" oils; Essolube engine oil 40.

The oils were tested under the following conditions:

RPM	2200
M.E.P.	5.6kg/sq. cm.
temperature, cooling water	50°
temperature, sump	100°

Runs were continuous for 72 hours. The following points were observed for evaluation:

1. Abrasion
2. Aging (viscosity rise)
3. Consumption
4. Piston ring sticking

The results of these tests are tabulated in Frame 909.

Frame 910-920. Progress report on motor oil tests in the Opel 1.3 liter engine February 19, 1938

The apparatus and method of conducting the tests are described, and the results are plotted in a series of curves. The oils are identified by code number.

ITEM 15. OCTANE AND CETANE NUMBER TESTS ON PRODUCTS

Frame 922-925. Fuel tests on the Jumo aircraft diesel engine March 16, 1943

A life test of a diesel fuel was made by Junkers. The test was performed under heavy load conditions. The following results were noted: Residue formation. A test with synthetic oil SS1502 (ester oil) and purely synthetic fuel from Ruhrchemie showed exceedingly low formation of deposits. Certain other combinations of lubricant and fuel produced much more engine carbon. The effect of the lubricating oil on combustion ring wear was very slight.

Frame 926-927. Discussion on knock testing, Ludwigshaven,
February 23, 1943

Frame 928-929. Differences in octane number determination between
the Benzol-Verband and Ruhrchemie
September 2, 1938

A sample from tank car No. 591,766 was tested by Benzol-Verband and assigned an octane number of 58.8; Ruhrbenzin tests had ascribed to the same fuel an octane number of 64. Cooperative tests were made to adjust the difficulty, two tests using the CFR engine and two the I.G. engine.

Frame 930. Supplement to the previous report which gives the results of tests on 3 additional samples.

Frame 931. Comparison of octane number determinations in different engines. A table.

Frame 932-949. Determination of cetane number
April 21, 1938

Cetane numbers were determined for 21 unhydrogenated and 14 hydrogenated fractions from Fischer-Tropsch synthetic oils. It was found that for both types of oils, the cetane number is dependent solely on the average boiling point designated as boiling index. Cetane numbers rise almost linearly up to about 300° and from that point remain at around 100 for both series. The cetane numbers of the unhydrogenated oils are somewhat lower than for the hydrogenated.

No comparison is possible between cetane numbers obtained by several different methods. 10 frames of tables and curves follow.

Frame 950-954. Dependence of octane number on aniline point
in cracked gasoline
March 21, 1938

Two test runs, in September and October, gave numeric confirmation of the previously observed relationship between octane number and aniline point. The results of the tests are plotted in a series of curves.

Frame 955-956. Octane number of Ruhrbenzin cracked gasoline
September 20, 1937

The octane number of an unrefined cracked gasoline was around 60.5, which might hold promise of a better value after a refining treatment. Frame 956 gives analytical data.

Frame 957-958. Improving the knock stability of primary gasoline, first by the addition of B.V. Benzol and second by the addition of B.V.Benzol and lead tetraethyl.
September 6, 1937

	Octane numbers (motor method)	
	I. Fraction up to 100°	II. Fraction up to 120°
Original gasoline	71.0	66.5
Original gasoline + 20% benzol	75.0	70.5
+ 30% benzol	77.0	73.5
+ 40% benzol	79.5	76.5
+ 20% benzol + 9cc $PbEt_4$ per liter	85.0	83.5
+ 30% benzol & 9cc $PbEt_4$	85.5	84.5
+ 40% benzol & 9cc $PbEt_4$	86.0	85.5

ITEM 16. REFINING PRODUCTS OF THE OLEFIN SYNTHESIS.

Frame 959-960. Minutes of discussion on high temperature refining of products, and the production of suitable catalysts for that purpose.

ITEM 17. OLEFIN SYNTHESIS = WATER GAS.

Frame 962. 20 pressure furnaces
December 9, 1943

A change of operation from a throughput of 1.170 cubic meters per furnace to 890 cubic meters showed considerable advantage in the increased production of valuable materials.

Frame 963-965. Processing 80,000 cubic meters with introduction of water gas synthesis
November 22, 1943

The operating conditions for this method are noted.

Frame 966-967. Processing 70,000 cubic meters of water gas.
November 17, 1943

This report supplements one which was submitted on October 29, 1943. The following subjects are discussed: 1) Turbocompressors; 2) Pressure synthesis; 3) Pressure condensation and activated carbon plant; 4) Low pressure synthesis; 5) Condensation (low pressure).

Frame 968-968B. Water gas recycle
October 16, 1943

Calculations are given for operating a battery of 62 furnaces for a water gas recycle synthesis.

Frame 969. Calculation of water gas recycle.
October 4, 1943 (practically illegible)

Frame 970-971. Considerations on converting pressure synthesis to water gas recycle, for gasoline production
May 12, 1943

Procedures are outlined for starting operations after a shut-down.

Frame 972-975. Processing and yield of gas from water gas synthesis
February 23, 1943

Three cases are proposed for the working up of the end gas from water gas synthesis. In Case I, using figures for normal pressure synthesis, with an input of 75,000 cu meters of water gas, the residual gas amounts to 37,000 cu meters. Of this, 20,000 cu meters can go to the conversion unit, producing around 27,000 cu. meters of converter gas. This, with the remaining 17,500 cu. meters, gives a throughput of 45,000 cu. meters of synthesis gas having a $CO:H_2$ ratio of 1:2. A one-stage operation is preferable with this type of material.

Case II. 18,000 cu. meters of the aforesaid converter gas are compressed at 10 atmospheres and passed through the CO_2 scrubber, where 6000 cu. meters of CO_2 are removed; combined with the rest of the gas, this results in an amount of 39,000 cu. meters of synthesis gas to be converted in two stages and at normal pressure.

Case III. The amount of gas required for conversion is passed through the pressure activated carbon plant and freed from CO_2 in a pressure scrubber.

Frame 976-989. Development from pressure synthesis to olefin synthesis
October 2, 1941

When in 1936 the attempt was made to develop a large scale plant for the production of motor fuels from carbon monoxide and hydrogen, it was realized that investigation of the chemistry of aliphatic hydrocarbons might lead to the discovery of a raw material for chemical synthesis comparable to the aromatics from coal tar distillates. This was particularly the case with the unsaturates, therefore the effort was made to produce the largest possible amount of unsaturated hydrocarbons.

By increasing the concentration of CO, it is possible to raise the olefin content, but in low pressure operation, difficulties arise with the catalyst. These difficulties can be overcome by diluting the gases or by recycling, but this solution necessitates the use of disproportionately large and expensive apparatus. The unsaturates produced have a rather low boiling range, while the higher-boiling unsaturates are of most interest as raw materials for further synthesis. It was then found that a relatively small increase in gas pressure resulted in a favorable effect on the boiling range of the products.

Medium pressure synthesis gave larger yields of liquid products. Primarily, larger amounts of saturated products are obtained by medium pressure synthesis than by normal pressure, however these form an excellent starting material for thermal cracking to product olefins.

In the operation of medium pressure synthesis, it developed that the gas components CO and H_2 were combined in a manner differing from that of normal pressure. The proportion of 2.18-2.2 hydrogen to 1C was obtained in the medium-boiling products of both types of synthesis.

It was found that in normal pressure operation, the conversion proceeded according to two different equations:

I. $1\,CO + 2H2 = H2O + CH_2$

and

II. $2\,CO + H_2 = CO_2 = CH_2$

In medium pressure synthesis, the conversion is almost exclusively that shown in equation I.

In order to accomplish the best conversion to the most desired products, a third stage was added, so that the proportion of $CO:H_2$ might be kept at the optimum level. In the first stage the $CO:H_2$ ratio is 1:1.55 in the second, 1:1.65, and in the third, 1:1.75. This results in a total conversion of 94-95%. In the end gas, there still remains a small amount of convertible gases while the remainder consists of inerts, mainly nitrogen, methane and carbon dioxide.

With the above-described multi-stage process, there is a considerable enrichment of olefins. In order to increase them still further, the end gas which is rich in CO is recycled with fresh water gas.

In technical experiments on this olefin synthesis, it was found that in the naphtha fraction (200-320°) 45% olefins could be obtained.

Ordinary double tube furnaces were used as catalyst chambers. The gas pressure was 10 atmospheres, temperatures were somewhat higher than heretofore, but an end temperature of 225° is sufficient. The catalyst was the usual cobalt catalyst.

The primary products resulting from the olefin synthesis just described can be further developed into a variety of materials, such as high octane aviation gasoline, lubricating oils, higher alcohols, fatty acids or detergents. The bearers of all these reactions are the olefins.

Frame 982-988 describe the first experimental operation of unit 10C, D with single pass, as compared with recycle unit 10A.

Frame 989 reproduces a series of curves showing results obtained with normal and medium pressure operation at Ruhrbenzin and Rheinpreussen.

Frame 990-991. Flow sheets showing water-gas synthesis status February, 1943.

Frame 992 gives the same information for December, 1941.

Frames 993-995 are sets of curves with practically undecipherable legends.

Frame 996-997. Production diagrams

~~Frame 998. Flow diagram of water gas synthesis, January 10, 1943~~

Frame 999. Manuscript notes.

Frame 1000. A series of time--product charts.

Frame 1001-1006. Preliminary results with injector circulation
December 7, 1940

Tests were made with units 131 and 132, using an injector pump to circulate the synthesis gas. The method of operating the units is described and the results are noted. In addition to the two units above named, injection pumps were installed in units in several more blocks.

Frame 1007-1018. Second Lurgi test, high temperature recycle with synthesis gas and cobalt-thoria catalyst.
January 23, 1939

A series of tests, covering the period from May to July 1938, was made to determine whether the second synthesis stage could be omitted in high temperature recycle operation. The catalyst was the normal cobalt-thoria product (100 CO, 15 ThO_2, 200 kieselguhr) used in the form of 2.5mm pellets. The furnace contained 35.5kg Co. The initial temperature was 200.4°. Reports of the individual test periods follow:

Periods 1 and 2 (25 days operation)

Gas charge, 1.13 cu. meters/kg Co/hr.; recycle ratio 1:2.22. At first a 97% conversion was attained, toward the end of the second period it was 92.5, giving an average conversion of 96%. In the second period, 15% of water gas was added in order to increase the olefin content of the naphtha. The $CO:H_2$ ratio was raised from 1:1.96 to 1:1.84. A certain increase in olefin value resulted, but the naphtha fraction in the total product was decreased, so the total change was slight.

Gas conversion was satisfactory in the first two periods, and would make possible the elimination of a second stage. Calculated to 75% CO conversion, the yield was 145% of normal.

The yield was an average of 149.4g/cu. meter ideal gas. The product has the following properties:

Naphtha (up to 195°C)	55% (vol.)	39.6% olefins
Oil (195-320°C)	31%	18.4% olefins
Paraffin 320°	14%	

Period 3 (14 days June 2-16, 1938)

Under otherwise equal conditions, the average CO conversion in this period amounted to 89.4%. The yield fell to 140.7g/cu. meter ideal gas. The product had the following composition:

Naphtha (up to 195°)	49.5%	(olefins 41.1%)
Oil (195-320°)	29.2	(olefins 19.8%)
Paraffin	21.3	

When the first three periods are combined, the following results are obtained during 39 days. With 93% CO processing, a yield of 145.6 g/cu. meter ideal gas was obtained. In these 39 days, the average CO conversion dropped from 98.5 in the first period to 89.2 in the third. With this operation, a second stage could not be eliminated. The cause for the decrease in conversion could not be definitely determined.

Period 5 (6 days, June 28 to July 4, 1938)

After the original $CO:H_2$ ratio of 1:1.93 had been reestablished in the synthesis gas, the yield increased again from 111g/cu. meters ideal gas up to 135. An average of 132g was obtained. The product had the following composition:

Naphtha (up to 195°)	63%	Olefins 36.8%
Oil (195-320)	24	Olefins 18.2
Paraffin	13	

The carbon monoxide conversion in this period was 90% and ~~was thus at about the same level as in period 3. Analytical degree~~ of liquefaction had been lowered about 9 units to 73 by the increase in temperature.

The same general type of information is given on the results of four more periods. The results of the entire series of tests are summarized as follows:

Operating with high temperature recycling (200°) with a normal Co-ThO2 catalyst and synthesis gas, at an average CO conversion of 93% a yield of

146g/liquid product per cubic meter of ideal gas was obtained during a 39 day test. The unit in these 39 days produced just as much liquid product as a normally operating unit with 75% conversion would yield in 56 days. The CO conversion at the beginning of the period amounted to 99%, and at the end to 89%. According to these results it is not possible to dispense entirely with a second stage in high temperature recycling. Catalyst life could not be accurately determined in the present series of experiments because of technical disturbances. If the first stage is operated until CO conversion has fallen to around 60%, with careful shielding a catalyst life of 3-1/2 to 4 months may be assumed, and perhaps even 5 to 6 months. The liquid products had the following composition:

Naphtha (up to 195°)	53%	olefins 40%
Oil (195-320°)	30	olefins 19
Paraffin	17	

In the untreated state, about 26% of this product can be used directly as a motor fuel with an octane number of 60, and about 22% at an octane number of 64. After chemical treatment, this amount rises to 45% and 40% by weight respectively.

By the addition of water gas (about 15%) to the synthesis gas, the olefin number of the naphtha is somewhat increased. However under present operating conditions the amount of naphtha decreased, so that less of the primary product could be used directly.

Increasing the temperature to 210°C proved undesirable because of the great increase in gasification. Allowing the naphtha to remain in the recycle gas is not recommended in high temperature recycle operation, since both the amount of gasification and the degree of saturation of the naphtha are increased thereby.

Frames 1013-1018. Tables and curves representing data from DVA synthesis No. 39. December 30, 1938.

ITEM 18. NEW RUHRBENZIN PROJECT FOR WATER GAS SYNTHESIS (1941)

Frame 1019-1020. Activated Carbon Plant for water gas synthesis
March 5, 1941

A brief note on a proposed arrangement of adsorber, dryer and heat exchange system which would result in a high butane yield and prevent any break-through of C_5 hydrocarbons.

Frame 1021-1026. New Ruhrbenzin project.
January 14, 1941

A conference was held on January 7, 1941, concerning possible developments at Ruhrbenzin. Increased cost of coal places this plant at a disadvantage when compared to installations which were connected with coke oven or brown coal tar plants. New equipment required would include 3 generators which might be made available in a period of 15 months.

Apparatus for recycling in medium pressure synthesis should be given priority in order to start the Oxo process. Some statements are made concerning the fuel and energy balance.

A summary of results from a 116-day run with pressure—water gas circulation at a temperature range of 193-209°, showed a CO conversion of 47.6%, H_2 conversion 74.6% and produced:

Naphtha	50.3%	(60.5% olefins)
Oil 200-320	25.9%	42.0% olefin
Paraffin above 320	23.8%	

The materials which might be obtained from the various primary products were discussed.

Frame 1027-1029 give the energy requirements for construction. Frames 1030-1040 are concerned with converters, fine purification, compressors—current consumption and cooling water—syntheses (pressure synthesis and low pressure operation) feed water, condensation, activated carbon plant, new distillation, fractionation and stabilization, lubricating oil manufacture, and refrigeration. In all cases present and proposed future conditions are noted.

ITEM 19. PRODUCT DISTRIBUTION AND OCTANE NUMBER OF PRIMARY NAPHTHA

Frame 1041. Product distribution and octane number of primary naphtha from Krupp Wanne-Eickel plant November 2, 1942.

The following product distribution of stabilized primary naphtha is given:

Boiling point		Octane number
up to 100°	29.5%	74
120	37	66
140	43	55
160	50	49
180	55.5	40
200	60.5	26

40,000 tons per year are available boiling up to 200°.

ITEM 20. NITRATION OF TOLUENE.

Frame 1042. Trinitrotoluene. October 19, 1942

It has been stated that a toluene plant in Krasnodar produced toluene from a Maikop petroleum.

After distillation of the toluene fraction, this fraction was nitrated to a mononitro toluene, ~~which was then separated from~~ the other hydrocarbons. After purification it was converted to trinitrotoluol.

Tests are proposed to determine whether, by using a specific concentration of nitric acid, it might be possible to produce mononitrotoluene without attacking the other hydrocarbons present.

Frame 1043-1050. Production of o- and p-nitrotoluene from crude technical toluene by treatment with highly concentrated nitric acid at elevated temperatures and in countercurrent.
October 1, 1943

In the production of nitrotoluene, it has been necessary to start with pure toluene, since some of the hydrocarbons which may be present in the crude technical product are attacked by the nitrating acid, with a resulting formation of tetranitromethane. Purification of toluene by close fractionation encounters the difficulty that isooctane has approximately the same boiling point and cannot be readily removed. Extraction with liquid SO_2 gives a better yield, but is expensive, and there is always the possibility that traces of isoparaffins may still be present.

A series of experiments was undertaken to determine whether it might be possible to use concentrated nitric acid at high temperatures, instead of nitration acid at low temperatures. It was found that nitration acid attacks isoparaffins more severely than does fuming nitric acid. After operating in laboratory apparatus glass apparatus at 90-110°C, it was decided to make tests on a larger scale.

The nitric acid was 83-90% concentration with a specific gravity of 1.47-1.49. The results of the tests showed that conversion is largely dependent on the HNO_3 concentration. The amount of nitric acid was constant in all experiments. With concentrated acid, 59% nitrotoluene was obtained, with 32% acid on the other hand, only 3%. The results of these tests led to a study of nitrating toluene in a continuous process. It was found that such procedure was possible, but only with highly concentrated acid.

~~Frame 1051-1053. Production of nitrotoluene utilizing nitric acid of~~ low concentration
August 28, 1944

In order to save highly concentrated nitric acid, tests were made on the nitration of a crude toluol having an isoparaffin content of 3-5%, using dilute HNO_3.

Small scale glass apparatus was used. The toluol and acid were heated to boiling for a specified number of hours. The excess of nitric acid amounted to 50-100% of the theoretical. When 40% HNO_3 was used, no appreciable conversion to nitrotoluene was observed. Using 48% acid, conversions of 35% were attained, and by increasing the acid concentration to 55%, a conversion of 50-53% was reached. Extending the reaction time brought some increase in conversion.

ITEM 21. DEHYDROGENATION OF HYDROCARBONS.

Frame 1054-1058. Dehydrogenation of low-molecular hydrocarbons, using Halogen. Experiments with heptane February 25, 1944

The dehydrogenation of heptane by means of bromine and chlorine was studied in the temperature range between 400 and 550°, using various catalysts.

Applying 70% of the theoretical amount of bromine (calculated upon quantitative conversion to olefins) the olefin yield in the liquid product amounted to 40-43%. 56% of theoretical bromine produced 30-35%. Carbon losses are between 0.3 and 0.6% by weight of the charge, the amount of cracked gas and cracked naphtha is about 2% by weight.

It was possible to convert the monobromides into olefins, the polybromides amounting to less than 2% are considered as loss.

The resulting C_7 olefins have the double bond in the 3-4 and 2-3 positions for the most part.

From the hydrogen bromide formed, 93-96% elemental bromine could be recovered by treating with air in the presence of catalysts.

Frame 1059-1063. Dehydrogenation of high molecular hydrocarbons (cetane) with halogens, particularly bromine, February 24, 1944.

Summary:

The dehydrogenation of high molecular hydrocarbons was studied, using chlorine and bromine.

Optimum reaction temperatures were around 485°C.

Of the catalysts tested, aluminum oxide (sinter corundum) and "Sterchamol" gave the best results with regard to olefin formation.

Olefin yields, referred to the bromine, amounted to a maximum of 60% with 100% of the amount of bromine necessary for complete conversion to olefins,; using chlorine, a conversion up to 50% was obtained. The reaction conditions were 100mm absolute pressure, and a contact load between 1000 and 1300 volume % liquid charge.

Analytical data showed that the olefins consisted, predominantly, of mid-position double bond compounds; iso-olefins were present to only a very slight degree.

Lubricating oils synthesized from the above noted olefins showed pole heights of 1.5 and 1.6, and yields between 40% and 60%.

The bromine can be almost quantitatively reclaimed from the hydrogen bromide formed using suitable catalysts at temperatures between 400 and 500°, with air introduced.

Frame 1064-1065. Dehydrogenation of low-molecular hydrocarbons, particularly hexane, heptane, octane and nonane. February 24, 1944

Parallel with the experiments on the catalytic dehydrogenation of high molecular hydrocarbons, an analogous series of tests was made using the lower molecular hydrocarbons. At first the same catalysts were used which had proved to give optimum yields with cetane; it was soon learned, however, that these specific catalysts were not of equal value in dehydrogenating short-chained molecules. Thereafter the normal aromatization catalysts were used. These consisted of 20% Al_2O_3, 18.5% Cr_2O_3 and 1.5% Na_2O.

Hexane seemed to be the most resistant to dehydrogenation; heptane gave fairly good yields, octane was more difficult and nonane again gave better olefin yields. The carbon loss was very slight in all cases. The entire series of experiments indicated, however, that dehydrogenation of hydrocarbons boiling between 60 and 150°C was not satisfactory with the catalysts in current use.

Frame 1066. Letter dated February 23, 1944, transmitting a report on the dehydrogenation of hydrocarbons boiling above 250°C.

Frame 1067-1070. The dehydrogenation of hydrocarbons boiling above 250° especially the dehydrogenation of cetane February 22, 1944

This report contains the results which were obtained in the catalytic dehydrogenation of C_{16}, C_{17}, and C_{18} hydrocarbons, to produce olefins.

Previous experience in aromatization was taken into consideration in regard to catalyst choice and manipulation. The fact that acid carrier materials such as silicates and pumice produced catalysts with scant aromatization activity led to the use of these substances as carriers for dehydrogenation catalysts. It had been found that small amounts of alkali decrease carbon deposition, while larger amounts suppress aromatization. It was also previously known that chromium oxide was the best catalyst for splitting out hydrogen. Most of the catalysts which were used in the dehydrogenation tests were prepared with these facts in mind.

The first experiments were made in a small reactor which could hold a catalyst volume of 30 cc. The throughput of 6 cu. meters/hour was too small to permit the drawing of an accurate balance. Several catalysts were tested and rejected before the remainder were examined in a larger unit which had a catalyst capacity of 250 cc.

The catalyst tube(18-20 mm in diameter) was placed in a vertical furnace 1,300 mm long; this was filled with catalyst for the length of 90cm., so that 250-270 cc of catalyst was present. The catalyst was disposed in a bed on quartz chips. The arrangement of apparatus and the method of operation are noted.

Final results are summarized as follows:

1. The dehydrogenation of higher boiling hydrocarbons, particularly in the boiling range of 280-310°C was studied.

2. The best values were obtained with catalysts which consisted of highly heated aluminum silicates which were intimately mixed with chromium nitrate and small amounts of copper and alkali nitrate, dried, and decomposed at 600°C.

3. At present, with single pass operation at 530°, a 20% olefin formation was obtained with a catalyst loss of 25-30% liquid feed. Under these conditions, the loss in cracked gas and cracked naphtha was 7-10%.

Frame 1071-1072. Production of olefins
February 22, 1944

Four possible methods were studied for the production of olefins, aside from the thermal or catalytic splitting out of hydrogen. These were:

1. Treatment of cetane in liquid or vapor phase with sulfur;
2. Treatment of cetane with hydrogen chloride and air or with air without hydrogen chloride;
3. Treatment with chlorine;
4. Treatment with chlorine and air.

1. Liquid phase treatment, refluxing the cetane-sulfur mixture resulted in almost quantitative splitting out of H_2S. However the iodine numbers were low, and considerable gas and tar formation occurred. Vapor phase treatment gave improved iodine number, but other physical constants of the product were unfavorable.

2. The use of different catalysts, such as bauxite, cobalt chloride, copper chloride and the like, produced no special differences when cetane-air or cetane-air-hydrogen chloride mixtures were passed over them. The desired reaction - production of nascent chlorine - $(2HCl + O = H_2O + Cl_2)$ could not be observed, instead, the oxygen reacted directly with the cetane.

3. Dehydrogenation with chlorine + S_2Cl_2 + a carrier gas produced at 300-350°C compounds which still contained combined chlorine. The method of simultaneous attachment and splitting out of chlorine gave better results, although it is possible that diolefins and cyclohydrocarbons may be formed.

4. Treatment with chlorine and air was accomplished in two stages. Accurate dosage of chlorine and oxygen gave good yields of olefins. The tests were discontinued because of the difficulty in obtaining supplies of chlorine.

Frame 1073-1081. Dehydrogenation of long-chained paraffin hydrocarbons February 12, 1944

The following plan was developed for solving the problem of olefin production from high-molecular hydrocarbons:

1. Develop catalysts and methods for the preparation of olefins without consideration of other reactions which may occur;
2. Investigate the nature of the olefins, with special regard to their applicability for use in Oxo and lubricant synthesis;
3. Study side reactions and if possible prevent or diminish them.

The chromites of metals such as zinc, thorium, copper, silver, nickel, strontium, barium and the like are favorable for use as catalysts.

Frames 1076-1081 reproduce tables and curves representing the data obtained.

ITEM 22. AROMATIZATION - PATENT CLAIMS

Frame 1083-1084. Aromatization catalysts, July 24, 1943

A note on the production of aromatization catalyst by decomposition of nitrates at definite temperatures.

Frame 1085-1086. Evaluation of U.S. patent 2184,235 on dehydrogenation catalysts - April 7, 1943

1087-1087B. Aromatization catalysts; patent disclosure October 30, 1942

A main patent (not further identified) describes aromatization catalysts which consist of chromium oxide - aluminum oxide with a small amount of alkaline earth. This disclosure proposes, as an improvement, the addition of small amounts of manganese. Such an addition causes a decrease in the deposition of carbon. This in turn permits easier catalyst regeneration. The proposed claim is for an alkalized chromium oxide - aluminum oxide catalyst containing in the finished catalyst about 1-2% of manganese oxide.

Frame 1088-1093. Process for the aromatization or dehydrogenation of hydrocarbons
August 13, 1943 (proposed patent application)

Claim:

Aromatization or dehydrogenation catalysts according to the main application (not identified) characterized in that aluminum oxide was used which had been precipitated with acid from sodium aluminate solution, under precise conditions of concentration and temperature, and immediately after precipitation, had been freed from any alkali by washing; thereafter a calcination of controlled duration and temperature produced a starch-like material which was plasticized with chromium nitrate and alkali, molded, and, after slow heating to a preliminary temperature, was completely calcined at a definite temperature.

Frame 1094. Catalysts.
December 9, 1939

A letter gives information on the preparation of a catalyst, with particular reference to the temperature relationships.

ITEM 23. AROMATIZATION REPORTS.

Frame 1097-1100. Four frames of photographs of the precipitates obtained in the manufacture of catalysts.

Frame 1101. Aromatization column
February 17, 1939

An aromatization column consists of 4 heat exchange units alternating with 4 catalyst chambers, having flange threaded connections in both directions. Introduction of naphtha vapor, flue gas, air and hydrogen takes place at the top of the uppermost exchanger. The catalyst chamber is a tube 80 mm in diameter and 200 mm long, provided with thermal insulation and heated externally by electricity. Temperature control is effected by thermoelements inserted through the insulation.

Frame 1102-1104. Aromatization tests with the 64-69° fraction of a Hungarian petroleum distillate
February 10, 1944

Attempts to aromatize a naphtha (64 - 69°) from Hungarian petroleum were unsuccessful. Then a study of the naphtha indicated that appreciable amounts of benzene and naphthenes were present. After these constituents had been removed by solvent extraction, the residual hexane could be converted into benzene, although considerable gasification and carbon deposition occurred.

Frame 1106-1107. Aromatization experiments with different fractions in the C_7 range of a Rumanian petroleum naphtha
August 21, 1943

In the search for a suitable raw material for the manufacture of aviation gasoline, tests similar to those on Hungarian naphtha were made on a Rumanian gasoline.

Frame 1108-1113. Aromatization of the C_7 fraction of active carbon naphtha, for forming toluene, using alkalized chromia-alumina catalyst Life test.
October 2, 1943

Life tests were made on aromatization catalysts prepared as follows: Calcined, alkali-free Al_2O_3 was mixed with the equivalent amounts of chromium nitrate, alkali nitrate, and—in one instance—manganese nitrate, gently heated and vigorously stirred with a little water to form a homogeneous paste. The paste was poured onto a plate, forming a thin layer about 5-8mm deep. After a 2-hour drying period at 150-175°, it was heated in a muffle furnace to 600° within 90 minutes, and then calcined at 600°. After they had been cooled, the sheets of catalyst were broken up (1-3mm grain size) and screened free of dust.

Descriptions are given of the apparatus and the feed stock used. The reaction time was 60 minutes, followed by 5 minutes shutdown, then 5 minutes blowing with nitrogen and 25 minutes with air, another 5 minutes with nitrogen and finally 5 minutes with hydrogen. Thus the regeneration time amounted to 45 minutes and the ratio of reaction time to regeneration time was 1.33:1.

The results show that within one year, almost 3600 hours of pure reaction occurred. Frames 1111-1113 give numeric data on these tests.

Frame 1114-1115. Aromatization tests with C_6 and C_7 fractions of Hungarian benzine
August 20, 1943

This is a report on work similar to that reported in frames 1102-1104.

Frame 1117-1124. Separation of heptane-toluol mixtures by distillation
April 28, 1943

Tests were made with a 50:50 mixture of heptane and toluol in an attempt to separate them so completely that no more than 0.2% heptane should remain in the toluene. A discontinuous bubble tower separation seemed desirable. The results are represented in 1 table and 4 pages of curves.

Frame 1125-1127. Second report on the aromatization of foreign naphthas.
November 20, 1942

Results are given of experiments with "Reitbrook naphtha". This naphtha was treated over a mixed catalyst comprising one volume of aromatization catalyst and one volume of cracking catalyst.

The results showed that aromatization with a mixed catalyst produced a motor gasoline which could be used without lead addition; the addition of 1.2 lead gave a product of almost aviation quality.

Frame 1129-1175. The dependence of the formation of aromatics and cracked gas upon the temperature of the reaction; also some special experiments in the scope of the aromatization program.
May 8, 1942

Several series of experiments were made using laboratory apparatus and procedure. The units were electrically heated, the catalysts were regenerated by sweeping with nitrogen, air and hydrogen. The composition of the catalyst was: Al_2O_3 76%, Cr_2O_3 22.6%. Ni 1.3% and MnO 0.1%. No molding or shaping of the catalyst was practiced.

The aluminum oxide was calcined at 700° before the manufacture of the catalyst, while chromium, nickel and manganese were applied in the form of their nitrates. The curves reproduced in Fig. 1 show the relationship between contact load and aromatization at different temperatures. It may be noted that with diminishing catalyst load (i.e. with increasing reaction time) the formation of aromatics increases.

Figure 3 shows carbon content in aromatization at constant temperature as dependent on the aromatic content of the liquid product.

Figure 5 shows the relationship of cracked gas formation to the aromatic content of the liquid product, or the reaction duration at different temperatures. With rising temperature, the amount of cracked gas is seen to increase sharply. A series of equations is developed, for calculating the formation of cracked gas, dependent on the amount of aromatics in the liquid product at different temperatures.

Additional experiments were made to ascertain the course of reaction time. It was found that aromatic yields dropped sharply with increased contact duration.

A considerable number of tables, graphs and charts give graphic representation to the results which were obtained from the experiments.

Frame 1176-1185. Aromatization experiments with foreign naphthas February 25, 1942

The properties are given of three petroleum distillates in the gasoline boiling range. These were studied to learn whether they could be converted into aromatic products which might be used as high-octane motor or aviation gasoline. Although several methods of conversion were tried, the results were not satisfactory.

Frame 1186-1193. The aromatization of iron catalyst recycle naphtha August 1, 1941

A study was made of problems which might arise in the aromatization of a recycle naphtha produced with iron catalyst. This product has a composition quite different from that of the C_7 fraction of active carbon naphtha, therefore difficulties were to be expected. The iron catalyst recycle naphtha contains appreciable amounts of alcohols which would be dehydrated by contact with the Al_2O_3-Cr_2O_3 catalyst; this would be detrimental since the aromatization catalysts are extremely sensitive to water. The presence of aldehydes, acids and esters might likewise be unfavorable to aromatization.

The feed stock was an iron catalyst recycle naphtha produced from December 1940 to January 1941 by the pressure unit. From this in a 1000 liter still, a fraction was cut with the boiling range of 80-200°. The following constants were determined:

Boiling	133°
D_{20}	0.732
Iodine No.	143
Neutralization No.	0.27
CO - number	14
OH - number	68
Saponification No.	5.1

Table I gives in essence the experiments which did not produce the desired results, i.e. the yields were too low, because of high carbon and gas formation.

Later some tests were made, in which the recycle naphtha was subjected to a preliminary treatment. These also were not satisfactory.

Table II shows a series of experiments which were made for the purpose of explaining the difficulties which had occurred. The first experiment was made with the C_7 fraction of regular active carbon naphtha; results were normal; liquid yield of 90%, 44% volume aromatics, 3.1% by weight of carbon.

Another test was made, adding methyl ethyl ketone to the C_7 fraction. This resulted in a decided decrease in liquid yield and in aromatic content, while carbonization losses increased about 10%.

A test was made with heptene having an iodine number of 222, (corresponding to olefin content of 85%), and boiling 92.5-93.5°. The results confirmed the opinion that olefinic products are difficult to aromatize.

In some of the experiments, a carrier gas was used, but no perceptible effect was achieved.

The experiments which produced the best results are contained in Table V. The feed stocks were subjected to pretreatment over calcined Al_2O_3 as used for aromatization, the reaction temperatures varied between 350 to 380°, the load between 50 and 100% liquid charge. The reaction product resulting from this pretreatment contained notable amounts of water of reaction. This may have originated from the dehydration of alcohols. The recycle naphtha, after this preliminary treatment, proved to be absolutely free from all oxygen compounds. After removing the water of reaction and briefly drying over $CaCl_2$, this product was introduced to the aromatization unit. At 460° the results were quite satisfactory with regard to liquid yield and carbon content.

Frame 1194-1198. Investigation of aromatized nonane
August 11, 1938

A sample of 450cc of aromatized nonane was subjected to fine fractionation in the 2.5 meter fractionating column. Separation into individual constituents is faulty. Therefore the fractions 92-118°, 118-134°, 134-140°, 140-150°, 150-160° and 160-170° were individually subjected to further fractionation.

After various tests, the following probable composition was ascribed to the sample of aromatized nonane (all percentages are by volume):

Aromatics	
3.5%	Toluol
5.0	Ethylbenzene and Xylols
23.0	(Propyl benzene, ethyl toluene, (Trimethyl benzene and higher homologs
31.5	

	Nonane and other compounds	
about	5.0%	unknown preliminary cut
	5.0	octane-octene
	57.3	nonane-nonene
	1.2	viscous black tar
	68.5	

Frame 1197 - Table; 1198 curves

Frame 1199-1200. Experiments on the aromatization of heptene and heptane
February 24, 1938

Apparatus:

An electrically heated oven, with 50 mm diameter inner tube, in which a 20 mm glass tube was placed, secured at both ends. This glass tube was equipped with ground glass connections at each end and was connected at the front end with the gasification apparatus and at the rear with a condenser. The gasification apparatus consisted of a 250cc flask with gas inlet and equipped with a burette from which the heptene was delivered drop by drop. Vaporization of the heptene was accomplished by heating. The primary receptacle collected most of the resulting liquid products. The liquid was suctioned off every hour in two condensers connected in-series, the first of which was cooled to -30° and the second to -190°, the remaining heptane and toluene fractions were retained. Here too were separated or dissolved all the cracked gases except H_2, CH_4 and small amounts of C_2H_6. By cautious warming of the condenser to 40°, these cracked gases were vaporized and captured in a calibrated flask over saturated salt solution.

Only the first two pages of a 50 page report are included in frames 1199-1200 of Reel 451. The report is concluded--after a few preliminary frames--in Reel 46.