

FILM STUDY GROUP
REPORT ON MICROFILM REEL NO. 39
Prepared by
THE ATLANTIC REFINING COMPANY

Mr. Hummer

SCANNING OF REEL #39
(Orig. Ident. Reel 7b)

U.S. Government Technical Oil Mission
Bag 3450 - Target 30/5.01 - Ruhrchemie A.G. Sterkrade-Koltan

SECTION 21 completed. COLLECTED EXPERIMENTAL WORK ON
LUBRICATING OIL SYNTHESIS

This section consists to a large extent of a series of short memoranda originating with Ruhrchemie. The frames are not numbered so that location of items would be wholly within sections. The practice begun on previous reels of stating the number of frames for each item will be continued, i.e. a figure within parentheses is given for each item.

Aug. 1, 1941 - Production of Oil from Recycle Naphthas made by Hoesch.

The two charge stocks had end points below 200°C. and olefin contents of 50 and 64%. These charge stocks were used directly or with previous treatment with sodium at 110°. The oil synthesis was carried out with "normal" catalyst, which is otherwise unidentified. The conclusion is reached that extensive synthesis is associated with low CO numbers. Highly olefinic charge, low in alcohol content, is desired. (5)

July 23, 1941 - Dechlorination of the Upper Layer.

The source of the sample or the use to which the information is put, is not specified. (3)

May 11, 1941 - Oil Synthesis, after Separation of the Naphtha into
Narrow Boiling Cuts, and after Purification with Sodium.

There was evidence of a relation between the boiling range of the olefinic charge naphtha and the pole height of the oil produced from this naphtha. The number of carbon atoms in the chain length was presumed to exert considerable influence on the properties of the recovered polymerized oil. Inasmuch as the acids, esters, aldehydes and ketones were known to be detrimental to the synthesis reaction, great effort was made to separate these away from the charge stock. Metallic sodium appeared favorable.

Comparison of the synthetic product made from narrow boiling fractions showed that with increasing chain length the pole height is improved, but the Conradson test becomes poorer. The molecular weight increases, but the aniline point and iodine number decrease. Treating with oxygen at 140° resulted in higher stability of the oils made from the fraction C₁₃ - C₁₄ in contrast to those made by polymerisation of C₆ to C₁₁.

On the basis of a single synthesis, it was shown that the acids, esters and aldehydes occurring as contaminant of cracked naphtha are harmful. Separation of these substances results in considerable improvement in the pole height, the Conradson test and amount of resin formation. The memorandum includes 14 graphs and 3 tables of data. (26)

Apr. 26, 1941 - Stabilization of Aviation Oil by Addition of
Phenothiazine before the Synthesis.

Phenothiazine, also known as thio-diphenylamine (O=C1N(C2=CC=CC=C2)C(=S)C3=CC=CC=C13) was known to be a good inhibitor. The disadvantage that it exhibits by separation in storage

can be diminished if one adds the inhibitor to the naphtha before the oil synthesis. The addition of small amounts of phenothiazine to cracked naphtha before the synthesis, did not suppress the formation of oil, although it lessened somewhat the speed of filtration and imparts some darkening to the finished oil. The process must employ the inhibitor in greatest possible purity to use as little as possible. It is necessary to use 0.1% phenothiazine in cracked naphtha to obtain the desired oxygen stability. Further experiments were in progress to determine the minimum necessary purity of the inhibitor, and the optimum conditions of use. (11)

Apr. 8, 1941 - Determination of the Oil Content in the First Runnings of Lubricating Oil. (1)

This memorandum refers to Dr. Goethal's letter of April 2, 1941. By a normal distillation in glass, there was found to be 44.7 weight percent of oil residue, and by rapid distillation (35 minutes in contrast with normal time of 75 minutes) there was found 50.1 weight percent of oil residue.

Mar. 28, 1941 - Oil K-1872 and K-1873.

Inspections of these samples are given, together with data after an oxidation test for 6 hours at 150°. (1)

Mar. 26, 1941 - Effect of Synthesis Duration. (8)

The naphtha was exposed to synthesis conditions of 95°C. in the presence of 2.5% $AlCl_3$ for 6 hours and for 20 hours. The yield of oil is slightly higher at the shorter exposure, although the residual olefin is also slightly higher. The differences in quality of the oil under the two contact times are minor. In addition to the use of aluminum chloride as catalyst, there is mention of an addition agent whose significance is not known, but reported only as numbers.

Influence of Naphtha Boiling Range.

The pole height of the oils resulting from synthesis of fractions, is shown to decrease from 1.58 for the fraction up to 70°, down to 1.48 for the fraction boiling at 185°.

Mar. 21, 1941 - Production of a Thin Distillate Oil Whose Viscosity at 20°C. is 1.7° and Which has a Flow Point Below -60°C. (6)

The distillate with desired properties was not made in full production, as the flow point was affected by paraffin. The laboratory succeeded in making the desired material from normal cracked naphtha, but attained a yield of only 2 to 4%. Increasing the synthesis temperature from 120 to 130°, resulted in yield of 6%.

Feb. 7, 1941 - Analytical Data on Lube Oil, First Running. (21)

Distillation of the so-called "upper layer" yields lube oil forerunnings which lie between the residual naphtha fraction and the residue oil with an Engler viscosity of 10°. It is the low viscosity distillate from a large plant and served for production of spindle oils or of diesel fuel II.

This forerunning was subjected to fractional distillation, and various analytical procedures applied. The systematic evaluation of the analytical data is made more difficult by the presence of impurities such as acids and esters.

Fractionation.

Tests were made for each 5°C. and the following data recorded on the fractions:

Viscosity at 50°
Pole Height
Molecular weight
Density at 20°
Flash point
Flow point
Dielectric constant
Refractive index
Aniline point

Molecular Weight

The molecular weight progressively increased from 159 to 391 with corresponding number of carbon atoms of 11 to 28.

Density

The plot of the density curve becomes progressively steeper, and at a viscosity of 1.6 is in the region of cyclic mono olefins. The lower boiling portion of the charge consists of aliphatic hydrocarbons and the higher boiling portion is naphthenic.

Flash Point

This property presents a continuously rising curve. The flash point becomes higher as the viscosity increases, and it is most apparent in sharply fractionated cuts.

Iodine Numbers

The iodine number increased from 14 to 67 as the temperature rose from 200 to 355°.

Flow Point

The flow point of the initial fraction was -68°C, and progressively increased in succeeding fractions to -11.5° and again fell to -46°

Dielectric Constant

There was a progressive increase in the dielectric constant with rise in boiling point of the fraction, and it may be inferred that the constant also increases with the percent naphthenes in the fraction.

Refractive Index

The values for refractive index when plotted against the boiling point of the fraction, exhibit a rather steep rise up to about 320°. This line is steeper than that accepted for paraffinic hydrocarbons and lies above it, although it is about midway between assumed values for paraffinic hydrocarbons and cyclo-olefinic compounds. This latter group shows very little change in the boiling range up to 320°. In other words the observed refractive index is a reasonable compromise between theoretical values for paraffins and cyclic mono-olefins.

Aniline Point

Showed a progressive rise with molecular weight from 77.4 at molecular weight 159, to 100.3 at molecular weight 391. This again is accepted as evidence of increasing naphthenicity of the higher boiling portion.

Feb. 4, 1941 - Investigation of two Deurax Test Naphthas. (8)

The charge stocks were cracked pressure distillates. Detailed inspections are given on these naphthas and an outline of the properties of the synthetic product is given. The conditions of synthesis and the catalyst used are not described. The only identifying numbers given are 3036 and 3045 but it is unknown whether these refer to catalyst numbers, to synthesis runs or to inspection laboratory samples.

Jan. 3, 1941 - Stabilization of Oil by Inhibitors. (12)

Phenthiazine and similar inhibitors are effective in some degree but are best employed by addition to the naphtha undergoing polymerization (see report of Oct. 30, 1940). Beta thionaphthol approaches phenthiazine in effectiveness. Beta naphthylamine imparts good resistance to oxidation; a mixture of naphthylamine and thionaphthol is not practicable as it produces much residue.

The use of 1,8-naphthylendiamine in amount of 0.3% is effective as a stabilizer, but imparts an objectionable odor and causes a dark red discoloration.

Anthraquinone-2 hydrosulphide is a yet stronger inhibitor. The following substances used in amount of 0.3% in oil 1596 were ineffective as oxidation inhibitors.

Di-p-tolylthiourea
Alpha-nitroso-beta-naphthol
1,2-naphthylendiamine

These substances used in large amounts cause discoloration of the oil. Tests were made with 8 different thio substances but possessed the disadvantage that they imparted corrosive sulphur to the product.

Dec. 19, 1940 - Resistance to Oxidation by Untreated Synthetic Oils. (3)

The test was upon samples from the Research Laboratory, having a viscosity at 50° of 8 - 10° Engler. The test consisted in exposing 175 grams of oil to 15 liters of oxygen per hour for six hours at 140 and 160°.

Dec. 3, 1940 - Aviation Oil 3033. (1)

The charge stock was the portion boiling above 150° derived from cracked, cold-pressed oil. The naphtha before the synthesis was treated with 2% Tonsil and inhibited with 0.3% phenthiazine. The catalyst was 5% $AlCl_3$. Inspections are given on the lube oil and the results of oxidation tests for 6 hours at 160°.

Nov. 13, 1940 - Refining of Used Catalyst Oils by Means of Lime. (5)

The text is not specific but the reviewer believes that the term "used catalyst oil" is probably that material extracted from the catalyst mass when the latter has lost its effectiveness and is to be discharged from the catalyst case. It has been proposed (April 22, 1940) to take the expended catalyst oil mass and decompose it with water, to which calcium carbonate was added, distill the separated oily layer from the asphaltic portion, purify or brighten the dark distillate oil by a treatment of aluminum chloride at 180° and then dechlorinate in the usual manner with zinc oxide and Tonsil.

The presently undertaken work was to explore the suggestion that the catalyst oil might be treated directly with calcium carbonate, or calcium hydroxide without distillation and after-treatment, deriving thereby a useful chlorine free oil. It was found that the dechlorination of the catalyst oil derived by decomposition with calcium hydroxide, lime or lime plus granosil, could not be carried out.

Nov. 8, 1940 - Investigation of a Dechlorinated Upper Layer from the Oil Operation on HCl . (2)

Several experiments were tried, one of which is as follows:

750 gr. of plant product was again treated with 2.1% Tonsil plus 1.1% ZnO for two hours at 180°. The total chlorine content was 16 mg. per kg. The corrosive chlorine compounds were found to be 0.7 mg. chlorine per kg., from which it may be inferred that the second treatment was quite effective.

Oct. 30, 1940 - Production of Oil Stable to Oxidation by Addition of Inhibitors before the Synthesis. (6)

The inhibitors used were phenthiazine ($C_{15}H_{11}N$), beta-thionaphthol, ($C_{10}H_7SO$) and beta-naphthylamine ($C_{10}H_7NH_2$). The results were quite encouraging.

Oct. 16, 1940 - Vacuum Distillation. Influence of Flask Size and Degree of Filling. (2)

When the flask was three-quarters filled, the distillate for a specified set of conditions was 28%. In contrast, when the flask was charged with a third previous amount the yield of distillate was 32%. It was concluded that a flask should be employed to receive an amount of charge stock as great as possible without danger of foaming over.

Oct. 15, 1940 - Production of a Special Oil for MM. (2)

This experiment was in accordance with discussions held between Hagemann and von Waltwitz, Aug. 6, 1940.

Oct. 14, 1940 - Production of Synthetic Oil with Index 120 from a Mixture of C₆ - C₇ with Higher Boiling Fractions from Cracked Naphtha. (5)

Four of the nine oils supplied had viscosity index of 120 and two of these had a flow point as low as -42°.

Sept. 11, 1940 - Preparation and Properties of Distillate Oil, Particularly with Viscosity at 50° of 1.7 and 2.50g.

The laboratory succeeded in producing oils of the desired viscosity with flow points of -65 to -60°. The yield was usually between 2 and 5%. The maximum was 8%, but in this case the flow point could not be reduced to the desired degree by distilling out the thin product accompanying the viscous oil.

Work upon the above distillate oils and their bright stocks gave a remarkably clear picture of the dependence upon the boiling range of the cracked naphtha charge stock, temperature, duration and method of synthesis. (17)

Aug. 23, 1940 - Increased Stability of Oils Treated with Inhibitors.

Inhibitors appeared a very interesting means for improving oil. They are readily dissolved and their use does not involve any considerable loss of oily substances by chemical reaction. Research showed that there were organic substances which had no adverse effect on the copper test, and did not impart odor to the oil, while at the same time imparting a higher resistance of the oils to oxidation. Of the many organic substances tried, three appeared especially useful. Alpha-Nitroso-beta-naphthol, beta-thionaphthol and phenothiazine. A modified procedure is mentioned in which the inhibitors would be mixed with the cracked naphtha before the synthesis. (22)

Aug. 20, 1940 - Preparation of a Sulphurized Oxidation Stable Oil. (22)

The problem of making a synthetic oil resistant to oxidation by treating with elementary sulphur is not simple, because other necessary characteristics are adversely affected. Often the sulphurisation step can be combined with the stabilising effect of AlCl₃ treatment by heating at 170° for three hours with the AlCl₃ and 0.1 to 0.2% sulphur, filtering, dechlorinating, heating without further addition to 250° for four hours and then distilling in vacuum. There is obtained an extraordinarily oxygen stable oil. The advantage is the use of simple agents such as elementary sulphur and aluminum chloride. One disadvantage is the evolution of H₂S in the process. Phenothiazine is quite costly and gives off much H₂S. To separate the unreacted material, the inhibited oil must be filtered cold. Even then it still separates on long standing as a jelly, and certain precautions have to be taken.

June 9, 1940. Examination of 3 Oil Samples. (2)

These oils were submitted to the writer for oxygen stability tests. One of them is identified as T85.

July 4, 1940 - Further inspections are given to supplement the memorandum of June 5, 1940. (1)

June 2, 1940 - Decolorizing Earth. Comparison of Tonsil with the Product of Ostdeutsche Keramik.

Parallel tests were run to decolorize treated oil, observing effects on synthetic aviation oil, clarification of an upper layer which has been treated, dechlorination of treated upper layers, etc. Tonsil was found to be superior. (7)

May 30, 1940 - Aviation Oil. Effect of the Character and Boiling Range of the Cracked Naphtha upon the Pole Height and Flow Point of the Synthetic Aviation Lubricant. (6)

The data shows that as the boiling point increases, the pole height decreases, and that in order to obtain oil with the desired pole height of approximately 1.60, the charge stock must be derived only by polymerisation of the higher boiling fractions. No consistent effect on flow point could be observed.

Apr. 30, 1940 - Experiment on Preparation of Aviation Oil.

This oil was to be prepared from the upper layer or residue oil, and needs a different amount of $AlCl_3$ in treating at 170 to 200°. The test was intended to explore:

- (a) The influence of charge stock on the properties of the treated oil, namely the oxygen aging test.
- (b) Whether through extreme aluminum chloride treatment, pronounced effect on properties could be noted. The oxygen stability is not improved, but the thermal stability is improved to some degree. (15)

Apr. 25, 1940 - Use of Additive in Compressor Oil to Prevent Foaming. (5)

50 gr. of compressor oil (viscosity at 50° is 11° Engler) is placed in a flask, and an air stream passed through it for 5 minutes at room temperature. The air is then stopped and after 5 minutes the foam level is measured. Little or no effect was imparted by 28 substances; 10 substances had a pronounced but not sufficient effect, while 4 substances or combinations were found to suppress foam formation effectively:

5% each pyrogallol and butyl alcohol
1% pyrogallol and 2% amyl alcohol
5% castor oil plus 2% caprylic acid
2% butyl alcohol, 1% pyrogallol and 2% benzyl alcohol

Apr. 25, 1940 - Examination of the Treated Fractionated Resid Oil.

Special attention was paid to making an oil with good oxygen stability. (6)

Apr. 22, 1940 - Report on Working up of Used Kontaktoll. (10)

Kontaktoll (catalyst oil), a more or less fluid or plastic mass, contains

decomposed aluminum chloride and aluminum chloride compounds of partly oily properties. By cracking or splitting off of Cl during the polymerization, the proportions of aluminum to chlorine/iron: 2.6 to 1: 3 in the discharged mass. It has a strong tendency to resinify; if a drop is placed on a glass plate for 3 days and exposed to air, it dries to a sticky mass. It is soluble in benzol, tetraline, chloroform, etc. Dioxan can be used to separate unreacted aluminum chloride from the used oils.

When sodium hydroxide, sulphuric acid and water are used, the aluminum chloride which may be present in the oil is destroyed.

A simple method was devised for treating of the unstable lube oil. Addition of granasil and heating to 220° yields a granular, light, easily filterable and transportable material. If the after-treating is carried out in a normal manner, one can separate the catalyst oil with a thin medium or diesel oil.

Apr. 2, 1940 - Information on Synthetic Oils. Research on Treated and Untreated Distillates. (9)

The lower boiling portions of synthetic oils ordinarily contain small amounts of paraffin. On vacuum distillation of the upper layer, this paraffin goes overhead with the low viscosity distillate, and results in raising the flow point of the spindle oil. The research answered the question as to how the proportions change when one treats the entire upper layer or that fraction boiling up to 300° in vacuum with the normal amount (0.75%) of aluminum chloride before the final fractionation.

Treating the upper layer with 0.75% aluminum chloride caused little change to boiling range, flash point and flow point, with the paraffin content. Only the cloud point was raised. There was some tendency for the flash point to rise and likewise the flow point. A floc separates, which upon dilution can be readily filtered off.

Mar. 1, 1940 - Observation on an 8° Treated Resid Oil after One Year in Storage. (15)

The original oils were made from charge stock having a viscosity at 50° of 8° Engler. The pole height was about 1.9 and the induction time was 10 minutes. This oil was treated with 1, 1.5 and 2% $AlCl_3$ and addition of 1% iron filings and 3% Kontactoil at 170°. The product was divided into several portions, one of which was not dechlorinated, or after the addition of inhibitors, was stored in glass flasks or canisters for a year.

Feb. 29, 1940 - Research Upon an 8° Untreated Resid Oil. (8)

A normal untreated motor oil from the plant was distilled into light, medium and heavy distillates, leaving 32% resid (bright stock). Inspection data for the several fractions is unusually complete.

Jan. 23, 1940 - Research on Extreme Decolorization of Treated and Untreated Oils with Subsequent Extraction of the Decolorizing Agent. (15)

This report upon a series of tests in which oils were treated with 50% Tonsil, etc. in place of the customary 5 to 10%, gave information which was not necessarily considered practicable, but threw light upon the nature of the synthetic oil being produced.

Decolorizing.

Oils treated with the normal amount of clay remained stable at 50°, but lose their stability when extreme amounts of decolorizing agents are used. At a higher temperature (180°) the stability was uniform. Samples passing oxidation test deteriorated in storage.

Untreated oils were stabilized by hot decolorization; increasing the decolorizing temperature from 180 to 235° imparted the same effect with 5 to 10% earth as with 50%. What reaction is responsible for this is unknown. The silicates do act not only as bleaching agents but also as catalyst with greatly extended surface.

Extractions.

By treating the filter cake resulting from recovery of the bleaching earth and by extraction with bensol-alcohol, a sulphur containing extract is recovered which can impart stability to untreated oil. Oil inhibited with such material when subjected to accelerated aging tests exhibited great resistance to pure oxygen. The practical significance is unknown; whether the recovery of this extract is uneconomical; whether this effect imparted by the black oils cannot be performed by sulphur containing inhibitors such as thionaphthal or thiodiphenylamine.

Reviewer's Note: At this point in the real are pages entitled "Volume 6, report on cracked naphtha and their oils". This is an enumeration of memoranda giving dates and titles in German. Presumably the list includes a number of memoranda which were a part of the preceding real.

SECTION 22. REFINING OF THE RECYCLE NAPHTHA FROM OIL SYNTHESIS BY MEANS OF COLD ZINC CHLORIDE SOLUTION

A report from the Oberhausen-Kolten Research Department dated Feb. 17, 1945. (12)

Recycle naphtha as produced over cobalt or iron catalyst, contained variable amounts of different alcohols. The OH number for cobalt type products is of the order of 20 to 50, while for the iron type catalyst the values are 200 and above. Removal of these alcoholic impurities may be done by dehydration in the gas phase over clay. However, the extraction of the hydrocarbon mixture by means of cold concentrated zinc chloride solution appeared to be a useful route. Without previous refining, polymerization of the recycled naphtha with a normal amount of aluminum chloride (2 to 3%) occurs on only a part of the olefins. The lower the OH number in the naphtha, the higher is the olefin decomposition. By markedly increasing the aluminum chloride (up to 10%) the deleterious effect of the alcoholic substances can be compensated. If a recycle naphtha is shaken with cold zinc chloride solution, the resulting product polymerises like a normal cracked naphtha.

The fraction of recycle naphtha boiling between 60 and 200° derived either by cobalt or iron catalysis was treated in the cold and in continuous equipment with concentrated zinc chloride solution containing HCl, substantially freeing the naphtha of alcoholic substances. The product oil was still further improved by neutralization of the naphtha at 200°. The properties of three resulting layers of naphtha, zinc chloride and alcohol were explored.

SECTION 23. POLYMERIZATION

This material is undated and has the appearance of being taken from a descriptive or general report covering a number of subjects as the result of a literature survey. The signature is that of Clar. (5) None of the material appears novel to United States Refining practice.

SECTION 24. PROPOSED RESEARCH PROGRAM ON LUBRICATING OIL SYNTHESIS

Memorandum of Sept. 25, 1944 and several undated penciled sheets outline the research program upon synthetic oils in the Kolten laboratories. (11)

SECTION 25. EXPERIMENTAL RESULTS ON LUBE OIL SYNTHESIS (16)

The material in this section consists of miscellaneous data and notes, probably used in the preparation of more formal reports. The material includes:

- (a) Inspection of fractions of cracked naphtha and recycle naphtha after fractional distillation.
- (b) Influence of chlorine content on corrosion of V2A by hydrochloric acid.
- (c) Carbon-hydrogen analyses of miscellaneous oils bearing research numbers in the groups 3700, 3600 and 3400.
- (d) Refining of recycle naphtha before oil synthesis.

SECTION 26. REPORT ON SYNTHESIS OF LUBRICATING OIL (110)

This appears to be a comprehensive report probably written in the period 1944 at Oberhausen-Kolten. The title page is missing but the table of contents is given:

- (a) Charge Naphtha. Examination, purification.
- (b) Result of Synthesis. Influence of boiling range, duration, temperature, aluminum chloride, catalyst oil, addition agent, bright stock fraction, polymer naphtha.
- (c) The Upper Layer. Working up, residual naphtha, dechlorination, vacuum distillation, comparison of results.
- (d) Aluminum Chloride After-treatment. The upper layer and the oils, catalyst oil addition, distillation, inhibitors, sulphur.
- (e) Various Improvements of the Finished Oil. Sulphuric acid.
- (f) Investigation. Residual naphtha, upper layer, lube oil forerunning, distillation, thermal stability.
- (g) Aging of the Oil.

Investigation of, and Purification of Certain Naphthas used for the Oil Synthesis.

The charge stocks were usually cracked naphthas derived by the Dubbs process from gas oil or cold pressed oil. As the structure of the olefin and the composition of the cracked naphtha has more or less influence on the analytical results obtained on the polymerised oils, they were first concerned with examination of such stocks. The charge to polymerization contained no primary product i.e. the end point of the cracked naphtha should be lower than the initial point of the charge to cracking. The presence of solid paraffin is undesirable because of its effect on the flow point of the polymerized recovered oil. The greater part of the hydrocarbons are straight chained; the straight chained olefins have the double bonds in different positions. The best pole height resulted from alpha olefins. The synthesis never attained a pole height corresponding to pure alpha olefins; but for C₆ compounds gave a value of 1.97 in place of 1.76, and for C₉ compounds, a value of 1.61 in place of 1.35. Impurities such as di-olefins, peroxide, water, organic sulphur, acids, esters, gum and alcohol are present in minor quantities, but exert a considerable effect. On standing in closed vessels in the dark, certain changes occurred as evidenced by discoloration and gum formation. Fresh naphthas were better suited to polymerization than those which had undergone aging in storage.

Inspection of the naphtha includes fractional distillation, determination of the olefin content by shaking with P₂O₅-H₂SO₄ according to Rattwinkel, where by alcohol and aromatics were eliminated. Density, refractive index, iodine number, Oil number, cobalt number, gum and dielectric constant were determined. Tendency toward polymerization was determined by shaking 20 cc naphtha in a Dewar flask with one gram AlCl₃ and measuring the heat liberated. The question

is raised, how much can the naphtha be improved as a charge stock by pretreatment. Distillation will remove gum resulting from storage. When substances are added to naphtha in storage of the type beta naphthylamine, etc. a precipitate is formed and should be removed by refining before the naphtha is used. It is believed that the most favorable material is freshly produced naphtha dried with calcium chloride in order to lessen the consumption of $AlCl_3$ and light treatment with Na_2CO_3 and activated clay. A high content of acid and esters, characterized by high NZ and VZ values is deleterious. Treatment with sodium carbonate or solid KOH is recommended. Recycle naphtha contains appreciable quantities of alcohol, and these necessitate zinc chloride treatment or depolymerization over activated clay. All forms of pretreatment should recognize that isomerization is not desirable and that the alpha mono-olefins are preferred.

Two methods appeared feasible: (a) Distillation of the naphtha over a mixture of magnesium and a little aluminum chloride, (b) the naphtha vapor, to which a little HCl is added, is passed over aluminum metal at 175° .

On account of their poor pole height, no technical use was found for some types of naphtha product: (a) activated carbon naphtha, as well as the primary product from Fischer-Tropsch synthesis which yields an oil with pole height 3.0, (b) when cracked naphtha vapor is passed over activated granall at about 250° , isomerization sets in which moves the double bond from the end to the middle of the chain, (c) polymer naphtha produced by the method of Egloff and Ipatieff from C_2H_2 at 230 to 260° and from 7 to 14 atmospheres over phosphoric acid, yields high octane product which was unsuitable for the oils.

Purification of the Recycle Naphtha before Synthesis.

Separation of alcohol in the cobalt recycle naphtha by passing the vapor over Al_2O_3 at 220 to 320° is performed on the fraction boiling from 60 to 200° . By this pretreatment the OH number in the naphtha is reduced to $1.0 - 0.5$, but isomerization which has an adverse effect upon the pole height sets in. Fresh catalyst is necessary, and the process is carried out as closely as possible at 230° , taking care not to separate out acid and soap impurities which form some protection against isomerization; within 8 to 12 hours the temperature is raised steadily to 300° and a constant temperature of 300 to 320° is held thereafter. A 50 day research period with a fraction boiling 60 to 200° at a throughput rate of 1.07 volume naphtha per volume of reaction space was employed. The naphtha had 65% olefins and an OH number of 24. The yield of oil was 52.5%, its viscosity at 50° was 11.5"E. The pole height was 1.6l and its OH number not more than 0.5.

Results of the Synthesis. Influence of Boiling Range, Duration, Temperature, $AlCl_3$, Kontaktol, Additives, Bright Stock Portions, Polymer Naphtha.

The synthesis formed two fluid phases, the upper layer consisting of saturated and unsaturated hydrocarbons, as well as the viscous polymer. Below, is the non-viscous layer called Kontaktol. Both layers are to a certain degree

soluble in each other. The upper layer contains some combined aluminum chloride. The reaction which is most vigorous with high concentration of olefins and the greatest activity of fresh aluminum chloride is theoretically complete when all the olefin has been decomposed. This condition is never reached, a certain part of the unsaturated hydrocarbons remain undecomposed. Intensive stirring is necessary, and dead spaces in which aluminum chloride or liquid may settle, should be avoided in the equipment. From each charge material, whether it is a mixture of wide boiling range or a mixture of $C_3 - C_4$ hydrocarbons, or individual olefins, polymers of different boiling range and viscosity will be found. In any case they will contain low viscosity products which must be separated from the desired residue oil (N-oil) with steam at 200° and 5 mm. pressure. The viscosity of these N-oils can be influenced within wide limits by the process conditions such as intensity of stirring, amount of aluminum chloride or the amount of Kontakoil employed, temperature, the duration of the synthesis, freshness of the catalyst, the purity or moisture content of the naphtha, and perhaps also the concentration of olefins.

The most potent factor which influences the decomposition of the olefins is the addition of $AlCl_3$. Aluminum chloride which at lower temperature favors polymerization, at higher temperatures tends to promote cracking and beyond this, dehydrogenation and isomerization of hydrocarbons. This complex character of aluminum chloride explains why no completely satisfactory theoretical classification of the polymerization reaction has been made.

If one carries out the reaction by the addition of small increments of $AlCl_3$, whereby the polymers formed are separated by distillation, then there is recovered a series of residue naphthas whose olefin content gradually decreases. These naphthas were examined for tendency to polymerize and the heat of reaction was measured. This is not as great as with the original naphtha but reaches a maximum, i.e. under the influence of certain by-products, resins are formed which lessen the reactive surface of the aluminum chloride and hinder the progress of polymerization. The catalytically reactive portion of the Kontakoil is a compound of aluminum chloride with the olefins. Whether this formation is necessary to the polymerization reaction, cannot be said with certainty. In place of $AlCl_3$, one can employ equi-molecular mixtures of activated aluminum metal and gaseous HCl . The most important variable is reaction temperature. At low temperatures, the polymerization action is slow but yields high viscosity oil. High temperatures favor rapid reaction and formation of low viscosity oils. Reaction temperature affects the viscosity and stability, as well as the iodine number of the product and to a lesser degree the oxygen stability and the pole height. The temperature changes in proportion to the time on stream. Cold synthesis gives a poor yield per unit of catalyst per unit of time, whereas hot synthesis necessitates only a short exposure. In hot synthesis a considerable variation in duration has little influence on the quality of the oil. Contrasted to this, synthesis at low temperature results in increase of viscosity at 50° as the run is continued.

The most important property of the oil, the viscosity pole height, apparently is determined by the boiling range, that is, the number of carbon atoms, and can be depressed, therefore improved, by addition of aluminum chloride in small amounts and short synthesis duration, as when small amounts of oil are formed and these are separated by distillation away from the principal synthesis material.

Numerous experiments were performed to explore the effect of contacting charge stock with catalyst. Continuous counter-current movement of the upper and lower layers is recommended. Of less practical significance but, however, of theoretical interest were two variations: the first employed a rapidly rotating device and the second employed a vertical tube containing the aluminum chloride in fragments and permitted the naphtha to move up or down through the catalyst mass. It was recommended that the charge be dry, neutral and degummed. The effect of additives such as sulphur, sulphur monochloride (S_2Cl_2) and inhibitors to the synthesis mixture was explored. They appeared suitable for the production of oxygen stable oil. Their presence apparently did not interfere with polymerization; sulphur reacted to liberate H_2S . This phase of the work is incomplete, but other studies were made employing HCl or Cl_2 during the polymerisation and the addition of activated Al, Zn, Mg and basic material such as colloidal clay. Dichlorethylene dissolves $AlCl_3$ compounds and lessens or postpones their drop in activity. Addition of H_2 or C_2H_4 effected no improvement. The addition of $SiCl_4$ to re-activate $AlCl_3$ was effective to some degree. The oxygen stability was not improved. Carbon tetrachloride exhibited the same effects to a lesser degree.

SECTION 27. AGREEMENT OF BOMBRIINI-PARODI-DELFINO AND RUIRGHEMITE ON SYNTHESIS OF $C_3 - C_6$ ALDEHYDES

Correspondence dated Nov. 19, 1941 embodied the terms of contract for licensing the Oxo process to the Italian Firm. The Oxo process is the production of synthetic substances from compounds with an olefinic double bond by reaction with carbon monoxide and hydrogen. It was said that Bombriini was interested in the production of $C_3 - C_6$ aldehydes for the manufacture of explosives. Contract called for a pilot plant with a capacity of 300 tons of aldehyde per year and a commercial unit with a capacity of 2000 tons of aldehyde per year. (10)

SECTION 28. REPORT ON FALL IN OUTPUT OF RUIRGHEMITE 1940-1941

Memorandum June 9, 1941 is for diminished output. The shortcomings were attributed to accumulated factors of weather, corrosion, and disturbance in the labor supply. (10)

SECTION 29. RUIRGHEMITE PROJECTION PROGRAM 1941-1942

This memorandum of July 25, 1941 is interesting because it enumerates the product and expected consumption of charge material. (7)

SECTION 30. ACETYLENE PRODUCTION BY FISCHER-RUHROHEMIE PROCESS (3)

Memorandum of Feb. 22, 1939 outlines the elements of acetylene production from methane or methane containing gases. It was said to have been discovered by Dr. Fischer and developed by Ruhrochemie. A large plant was being built. Methane was decomposed at 1400° and unstated vacuum to yield acetylene and hydrogen. If the charge stock contained higher hydrocarbons such as ethane and propane, as much as 10% would not be reacted in the desired manner, but increased the tar yield. A second step comprised the washing out of acetylene from the reaction gas and its concentration. It was said that in some instances it is possible to combine the second step with the first directly.

About 55,000 cubic meters of reaction gas is produced daily with the following analysis:

<u>Component</u>	<u>Percent</u>
CO ₂	0.4
C ₂ H ₂	11.0
H ₂	79.1
CH ₄	5.1
N ₂	4.1
Misc.	0.3

When making gas of the above composition the cost was equivalent to 360 RM per ton C₂H₂ per year. The following utilities were necessary per kg. of acetylene: Heat, 9,000 calories; power, 2.2 kwh.; water, 1.5 cu. meters at 25°C.; methane, 3.9 cu. meters.

SECTION 31. FLOWSHEET FOR COBALT CATALYST MANUFACTURE

This information is not supported by text. It is extremely complicated by recycling, and as there is no means of determining the principal flow, maximum usefulness must await finding of descriptive material.

SECTION 32. FLOWSHEET FOR IRON CATALYST MANUFACTURE

This flowsheet dated Mar. 24, 1941 shows the sequence of steps without revealing the quantities and process conditions involved.

SECTION 33. CATALYTIC CRACKING AND AROMATIZATION

The first memorandum (3) in this section, dated August 31, 1942 gives a generalised description without supporting data. The process was developed by Ruhrochemie and was applicable to synthetic hydrocarbons of the Fischer-Tropsch type. Stocks boiling above 100-120° may be used; it is said to be distinguished from other processes of a similar nature by the very simple construction.

Using charge between 200 - 500°C., there is obtained a 32% yield of gasoline boiling between 60 - 165° which after the addition of 1.2 cc. TEL has a CFR octane number above 100 and iodine number of 0. The aromatization of hydrocarbon of the Fischer type was said to be possible, and this process may be used for treating C₇ hydrocarbon to produce toluol. The material in this section is without significance

A memorandum of Sept. 5, 1940 appears to be a continuation of the preceding information. It includes a process flow diagram and the text refers to the numbered items on the diagram. (7) The catalyst is activated clay, commercially known as granusil, tonsil or superfiltrol. The catalyst is activated with small amounts of cobalt (0.8%) and phosphoric acid (1-2%). Synthetic catalysts may also be used, and one is mentioned in which the proportion of Al₂O₃ and SiO₂ was 1:4 with an added amount of 1% BaO.

SECTION 34. LINSEED OIL SUBSTITUTE

A memorandum July 3, 1941 lists two pages of oils which may be substituted in part for linseed oil, and notes their principal occurrence and composition. Several pages are devoted to discussion of synthetic substitutes for linseed oil and the memorandum is closed by a tabulation of literature references chiefly in the period 1936 to 1939. (11)

A second survey of the technical and patent literature relating to the synthesis of drying oils is given, apparently closing out a project begun May 1941. The reviewer does not believe that the film contains information not available or not already known to the American vegetable oil, paint and lacquer industries. (12)

SECTION 35. REPORT ON OPERATION FOR FEB. 1943

A memorandum of March 25, 1943 gives production figures on primary nitrogen, ammonia, nitric acid and ammonium nitrate. Power consumption and catalyst requirements are mentioned. During this period, the synthetic catalyst plant was in operation to produce for the requirements of licensees. (1)

SECTION 36. REPORT ON COBALT SITUATION

Copy of letter March 24, 1943 to Braunkohle Benzol apparently assuring them that there will be an adequate amount of cobalt catalyst available. (3)

SECTION 37. COST OF MECHANIZATION

This one page memorandum Aug. 18, 1942 addressed to Professor Martin apparently refers to a catalytic process for increasing the CH₄ content of gas at the expense of volume of H₂ and CO, thereby increasing the heating value. The overall cost of the gas was estimated 9.1 pfg. per cu. meter of gas. There is not sufficient data on this isolated piece of information to assess the value of the step.

SECTION 38. TWO LETTERS ON THE OXO PROCESS (2)

The first piece of correspondence between Endres and Martin, dated Mar. 15, 1943, touches upon the following subjects:

In the reaction of CO and H₂ on unsaturated hydrocarbons for the production of alcohol, when the double bond is in the 1,2 position, it is possible to make higher molecular weight normal alcohol. There is interest in the possibility of synthesis of aliphatic alcohol by other means; normal dodecyl alcohols are necessary in the manufacture of highly bactericidal quaternary ammonium salts, which are the basis of modern surgical disinfectants. As long as cocoa fat was available, there was no difficulty in separating out the dodecyl alcohols in pure form. Today, there is available only mixtures of isomeric alcohols which are formed by reduction of the fatty acids made by paraffin oxidation. The writer appeals to Prof. Martin for assistance in obtaining information and samples which may be processed.

The second letter, Mar. 23, 1943, is a reply to Endres. Martin does not offer him much hope, saying that the Oxo plant will be in production in the Spring, but the fatty alcohols are likely to be found only in mixtures, as for example, C₁₃ and C₁₄. He suggests that Endres get in touch with Oxo Gesellschaft when the new plant is in production.

SECTION 39. SYNTHESIS OF HYDROCARBONS FROM CO₂ AND H₂

Martin to the Minister of Arms & Munitions, Feb. 12, 1943, explaining that direct production of hydrocarbons from CO₂ and H₂ does not seem feasible. The CO₂ must first be reduced to CO. Second, the temperature necessary for reduction of CO₂ with H₂ is higher than that employed for the synthesis of hydrocarbons. The reaction is not complete, and the resulting reaction product is a mixture of the carbon oxides. All work done to date has been on a small scale laboratory experiment and further investigation would necessitate the use of a semi-works plant. (2) A mixture of CO₂ and H₂ may be used in synthesis of methanol, but the further employment of such alcohols to produce hydrocarbons did not appear feasible.

SECTION 40. REMOVAL OF ORGANIC SULPHUR FROM GAS

This memorandum (3) on Feinreinigung is dated Feb. 6, 1941 but is unsigned. After removal of H₂S from synthesis gas, there remains 10 to 20 gr. of organic sulphur per 100 cu. meters (about 60% CS₂ and 40% COS with a small amount of mercaptan). The decomposition and absorption of this sulphur is described. Granular iron oxide which has been treated with alkali, is the principal reagent. At 200-300°, organic sulphur reacts with iron oxide to form FeS, which is oxidized to iron sulphate by the O₂ content of the water gas. If the water gas does not contain sufficient O₂, some is added before the Grobreinigung so that the content entering the Feinreinigung Plant is 0.1-0.2%. Cyclic sulphur is only mildly decomposed at 200 to 300°. Thiophene occurs only in carbonization gas, mercaptans will be absorbed in the Feinreinigung and they must be eliminated as much as possible. The gum formers are destroyed at 1100°. By-product gas,

such as from brown coal which has not been subjected to high temperatures, is handled with difficulty. Residual H_2S is completely removed in the Feinreinigung. The Reinigung mass can receive up to 10% sulphur by weight. It is necessary to increase the amount of O_2 in the gas and to raise the temperature slowly from 200 to about 310°. The Reinigung tower must be built simply and with a view to easy emptying of the depleted contact mass. For a thruput rate of 20,000 cu. meters of gas per hour, two towers, each with 65 tons of Reinigung mass are employed. When the sulphur content of the first tower reaches 10 to 11%, the second tower now becomes the first in a series and the newly filled tower now becomes the second of the series. The gas coming from the first tower is cooled to afford a temperature 25° lower in the second tower than in the first. The gas after the second tower has a temperature of 100 to 190°. The effectiveness of purification is illustrated by the following figures:

Inlet to first tower contains 0.4 gr. H_2S per 100 cu. meters plus 14 gr. organic sulphur. Leaving the first tower, the respective figures are 0.1 and 1-2 gr. per 100 cu. meters. Leaving the second tower the respective amounts of H_2S and organic sulphur are 0.1 and 0.2 gr. per 100 cu. meters. The memorandum mentions a sketch of the Feinreinigung plant which does not appear with the text.

SECTION 41. A PRESSURE FLOW METER

A memorandum of Nov. 21, 1944 and sketch describe an instrument capable of measuring gas volumes at 250 atmospheres. The principle involved seems to be the movement of a magnetized index actuated by change in mercury level of the reservoir with change in flow. (2)

SECTION 42. ACCOUNTS OF RUN WITH IRON CATALYST

This section is composed of a number of memoranda on topics not necessarily related.

Nemo. Aug. 30, 1943 - Synthesis of a Gasol (C_2-C_4 hydrocarbons) in paraffin formation. Analysis of the product gas, calculated yields on the CO and H_2 charge are given. (1)

Nemo. Aug. 20, Aug. 11, 1943 deal with tests upon paraffin-forming iron catalyst described at some length. (18)

The catalyst composition is described, but not the mode of manufacture. Operating conditions, the product, extraction and emptying of the spent catalyst case are described. The catalyst is identified as #1775. These two memoranda should be useful to those interested in the synthesis of paraffins.

Nemo. May 29, 1943 gives additional analyses of C_2-C_4 fractions. (3)

An undated memo. transmits a report of Dec. 22, 1942 on the subject of extracting and drying iron catalyst. (2) This latter describes an experiment on catalyst #1798 used in oven 11 for a period of 45 days. The oven was sub-

jected to extraction 5 times with heavy naphtha at 140°. Inspections of the naphtha are given after each extraction. The drying of the catalyst mass was performed at 200°. The oven was heated for two hours with superheated steam at 200° and 0.3 atmospheres, during which time an additional quantity of product was driven out. The naphtha content of the catalyst after the extraction step was estimated to be 56 volume percent. To eliminate the small amount of moisture from the catalyst, nitrogen at 200° was introduced. The temperature is dropped to 120°, the catalyst is saturated with CO₂ and the oven is emptied in the shortest possible time by jarring gently. The catalyst showed little disintegration and was not pyrophoric. The extracted and steam dried catalyst is no easier to moisten than a fresh catalyst or one containing paraffin. The memo. describes additional work: used catalyst was shaken with an equal volume of moistening solution (aqueous). A 1% solution of KOH or NaOH gave extensive wetting. Extraordinary wetting was said to have been obtained with a 0.1% Nekat solution BX.

An undated memo. (2) addressed to Professor Martin gives inspection and brief operating conditions upon a test conducted for SICS (Italian)

Memo. Nov. 9, 1942 discusses yield and product resulting from synthesis. (3)

Memo. Nov. 10, 1942 comments upon the preceding. (4)

Memo. May 19, 1942 summarizes results of a 120 day run on oven 14A using catalyst 1552. (2)

Memo. Mar. 18, 1942 - written by Bahr and entitled "Observation on Iron Catalyst for Medium Pressure Synthesis". This memorandum appears to be of interest as affording an insight upon the manufacture of current catalyst. It is divided into four parts: (a) the significance of the "residual alkali" and "activating alkalies" in the manufacture of precipitated iron catalyst; (b) reduction of the iron catalyst; (c) temperature relationships in iron catalyst; (d) practical results or deductions from the temperature relationship in iron catalyst synthesis. (7)

Memo. May 9, 1942 - Report (15) on run of oven 11, 10th filling. Two letters, Mar. 17, 1941 and Nov. 17, 1941 deal with the use of residual gas coming from the iron catalyst synthesis process to be used as commercial city bendout. (4)

Memo. Oct. 7, 1941 deals with catalyst SL427 used in naphtha synthesis. (2)

Memo. Dec. 12, 1940 reports on synthesis using water gas in a recycle operation. (3)

Memo. Sept. 10, 1941 supplements report on run of oven 11, 9th filling. The same subject matter is discussed in memo. of Aug. 22, 1941, which because it has more data than usual, may be presumed to have had greater significance in the eyes of the investigators. (13)

Memo. Mar. 21, 1941. CO₂ Washing in Iron Catalyst Synthesis. Discussion of CO₂ removal by water in direct cooling of the reaction product. (2)

Memo. Dec. 5, 1940. Water gas recycle over precipitated iron catalyst. (1)

Memo. Nov. 29, 1940. Water gas recycle with catalyst precipitated by KOH (oven 11, 7th filling). (7)

Memo. Nov. 20, 1940 - character of the synthetic product from oven 11, 7th filling. (2)

Memo. Nov. 18, 1940 - Research on Recovery of Paraffin Gases with iron catalyst. (12)

Memo. Sept. 17, 1940. Summary of the products on experiment with water gas in recycle operations, using precipitated iron catalyst. This memorandum also relates to oven 11, 7th filling. (3)

Memo. of Sept. 3, 1940 gives a tabulation of values obtained in oven 11 with water gas and using 5 catalysts. The first was precipitated type in which the proportions of Fe, Ca and Cu are 100, 30 and 5 respectively. The catalyst was impregnated with 1/20 normal NaOH. The sample was unreduced but was ground with NaOH. The second catalyst was also precipitated and contained Fe, Cu and Al in proportions 100, 4 and 5. The base was 120 parts kieselguhr. Material was reduced and precipitated with KOH. The third catalyst contained Fe, Cu and kieselguhr in the proportions 100, 5 and 10 and is designated as Luxmasse and was unreduced. The fourth catalyst was the same as the third except that it was reduced. The fifth catalyst was precipitated on kieselguhr with NaOH. The proportions of Fe, Ca, Cu and kieselguhr are 100, 10, 5 and 100 respectively. The sixth catalyst resembles the fifth except that KOH was used as the precipitating agent. (4)

There are several pages in the reel at this point, whose relation to the other memoranda and reports is not identified.

Memo. Sept. 7, 1940 reports results upon processing water gas in oven 11 using catalyst in which the Fe was precipitated by NaOH. The catalyst composition was Fe, Ca, Cu and kieselguhr in the following proportions: 100, 10, 5 and 100. The purpose of the experiments was (a) comparison of results in the same oven with the use of Luxmasse as catalyst and (b) the influence of recycle rate on the effectiveness of reaction and the composition of products. This new catalyst did not measure up to Luxmasse. The effect of recycle rate showed no consistent trend. (6)

Memo. Sept. 11, 1940. General Remarks on the Research to Date with Iron Catalyst. Transmitted by note of the same date addressed to Dr. Hagemann, contains a summary of research with iron catalyst written by Pfetsing. It is accompanied by several penciled graph sheets which illustrate the trends observed. (12) The material in this memorandum appears to be the same as reported in memo. of Sept. 3, 1940 (above) but because of the greater detail in the memo. of Sept. 11, this source is of first interest.

Memo. Aug. 22, 1940 - Water Gas Recycle with Lurgi Iron Catalyst.
Experiments were made with a reduced Lurgi catalyst of the following composition: 100 Fe, 4 Cu, 5 Al, 120 Kieselguhr. The water gas recycle rate was 1: 1.9 and the temperature was brought to 240° in 24 hours. It was shown that the Lurgi catalyst provided good synthesis of liquid products, although not giving the whole life effectiveness of the ROH catalyst. Interruption to operation is very detrimental to the catalyst life. The experiment is identified as oven 11, 3rd filling. (5)

Memo. July 10, 1940. Supplement to report of June 26, 1940. (below)

Memo. June 26, 1940. Report on Water Gas Research with Iron Catalyst at 20 Atmospheres. This work is identified as oven 11, 5th filling. (15)

Memo. Feb. 29, 1940. Comparison of reaction of synthesis gas and water gas with cobalt and iron catalysts. Three parallel experiments were performed: cobalt catalyst with synthesis gas; same catalyst with water gas; and Lurgi iron catalyst on water gas. The results may not be strictly comparable because of certain difficulties in effecting material balances and because the operating conditions are not necessarily optimum, but it may be presumed that the iron catalyst was considered a probable means of supplementing cobalt catalysis. (3)

Memo. Apr. 17, 1940. Data for Oven 11.

The charge to oven 11 on Mar. 29 was iron catalyst in fibre (?) form. The oven filling is unidentified. (3)

SECTION 43. REPLY TO QUESTIONNAIRE OF IRON CATALYST PROCESS

The origin of the questionnaire we do not know, but appeared to be associated with a paraffin project. Memo. May 27, 1943 addressed to Professor Martin says that the reply to the questionnaire is based upon run data from oven 14A, 3rd filling, covering a period of 120 days on stream. (11)

SECTION 44. FATTY ACIDS VIA OXO ALDEHYDES FROM IRON CATALYST PRODUCTS

Note of Feb. 2, 1943 transmits to Martin a memo. of Feb. 1 concerning recovery of fatty acids by iron synthesis. There appear to be two competing processes: oxidation of paraffin gas (320-460°) in accordance with the program of MOB (Mineral-Ölbau G.m.b.H.) and the direct oxidation of aldehydes recovered by the Oxo process. The calculations for the latter process were based on an assumed input of 50,000 tons primary product per year to yield:

Fatty acids	-	12,250	tons
Fuel gas	-	6,170	"
Naphtha	-	17,790	"
Diesel oil	-	9,950	"
Heavy oil	-	3,000	"

The calculations were based on those of Dr. Meyer Oct. 13, 1941 and data from ROH in oven 14A, 3rd filling. The average yields for oven 14A were:

C ₃ - C ₄ Fuel gas	-	10.5%
Naphtha up to 200°	-	36.5%
Oil 200-320°	-	15.5%
Soft paraffin 320-460°	-	18.5%
Hard " above 460°	-	19.0%
Olefin content of naphtha up to 200°	-	66.0%
Olefin content of the oil 200 - 320°	-	52.0%

Memo. Jan. 31, 1943 - Report of MOB on the Production of Synthetic Fat from ROH-Fischer Paraffin Jan. 15, 1943. Summary of calculations showing raw material, power requirements, plant costs, steel requirements and product yields for this proposed MOB installation. Several pages of manuscript are, apparently, the original calculation sheets for some of these memoranda.

Memo. Oct. 13, 1941 - Recovery of Fatty Acids by Oxidation of the Aldehydes made by the Oxo Process from Primary Products of Ruhrchemie Iron Synthesis. The calculations are summarized to show:

- (a) Primary products C₃ - C₄, Naphtha, Heavy Oil, Soft and Hard Paraffin.
- (b) The result of cracking the soft and hard paraffin, mentioned above, to yield heavy oil, naphtha, C₃ - C₄ hydrocarbon, with 5% loss.

The charge to the Oxo synthesis is 17,000 tons primary Diesel oil with 70% olefins and 14,400 tons cracked heavy oil with 65% olefins. From this combined charge containing about 21,000 tons of olefin which is reacted with CO and H₂, there results about an equal weight of raw aldehyde, or about 17,000 tons of pure aldehyde which is then subjected to oxidation for production of fatty acids.

Costs are calculated for the various steps from which it is deduced that a plant to make the fatty acids through the route of the Oxo process is cheaper, both in capital cost and per unit of fatty acid. (5)

Memo. Aug. 29, 1942 enumerates chemical requirements and costs in making pure fatty acids according to the new "B" process. (2)

Memo. Jan. 15, 1942. Basis for reply to letter of Dr. Altpeter. This material (2) is in the same vein and reaches the same point as memorandum of Feb. 1, 1943 on the same subject, discussed above.

SECTION 45. RUSYN IRON CATALYST PROJECT

The term Rusyn probably was applied to a project intended for construction in Russia and the several memoranda indicate that the work, which is largely calculations and estimates, was carried on in conjunction with Gutehoffnungshütte. (28)

SECTION 46. AREZZO IRON CATALYST PROJECT

The location of this Arezzo project is not stated but from the material it is inferred that this was a joint affair between Lurgi and Ruhrchemie. The most important document is a comprehensive report July 17, 1942 which describes the plant equipment and processing for the production of 25,000 tons per year of finished synthetic product. The plant included water gas generators, holder, compression plant, CO₂, scrubbing, purification plant and the synthesis unit itself. Assumed compositions of charge, intermediate and final products are stated, and directions given for operation of the several units. The catalyst consisted of Fe, Cu, CaO and Kieselguhr in the following proportions: 100, 5, 10, 150. The more than usual detailed instructions on catalyst manufacture lead to the presumption that the Arezzo plant was to be wholly self-contained. There are a considerable number of original graphs and data calculation sheets apparently used in setting up the final specifications for this project. (73)

SECTION 47. ENGINEERING DRAWINGS OF OVENS AND FLOW SHEET (52)

The following drawings are exhibited: RCH #2.KA20.101 preheater of 16 square meters heating surface for use at 12 atmospheres.

Hammesmann #63013 catalyst oven with leaved sheets (drawing bears the notation "oven 9").

Drawing XI-15672 Cooler.

Drawings apparently submitted as competitive bids by Krupp and Hammesmann.

Lurgi #2FD/23 generalized flow sheet of high pressure research plant for Ruhrchemie.

Ruhrbenzin #ZM103/85 - Assembly (plan and elevation) of high pressure plant.

Ernst Haage #RB191 - Flow diagram of high pressure synthesis plant.

Mannesmann #RW28811 - Catalyst oven cover.

Ruhrbenzin #ZM106/29 - Generalized flow sheet.

Lurgi #OFT/29 - Drawing untitled but appears to be details of oven.

Lurgi #OFT/28 - Generalized diagram showing flow of material in plant Hoesch.

Ruhrbenzin #ZM100/1646 - Test catalyst ovens (bears the notation "Oven 14").

Ruhrbenzin #ZM103/96 - Inlet tube for #3 oven. For attachment of heating elements.

Ruhrchemie #DVA89 - Oven 15.

Ruhrchemie #DVA93 - Catalyst Oven 16.

Ruhrchemie #DVA58 - Reaction vessel - oven 17.

Ruhrchemie #DVA62 - Schematic flow diagram of high pressure plant 3FT.

Ewald Berninghauf #XI 15470 changes to the cool oven.

Ruhrchemie #DVA5 - New construction research oven.

Ruhrchemie #DVA10 - Valve and instrument location for a part of the catalyst plant.

Ruhrchemie #DVA15 - Flow diagram of research plant.

Ruhrchemie #DVA29 - Some oven details.

The above enumeration of drawings found in this section is unsatisfactory. Reviewer believes that many of the sketches represented proposals of equipment manufacturers; that there is no certainty as to which design is actually in effect at the time of the sustained production.

Ruhrcemie A.G. - Sterkrade-Kolten

SECTION 1. PATENTS

Note by Reviewer: Where possible, the material in this section will be referred to by the disclosure number, as for example, R620 following. (A list of disclosures appearing in Reel 39 has been appended to this report)

R620 - June 6, 1942 - Process for operation of exothermic catalytic oven, especially for performing the catalytic hydrogenation of CO.

The process employing catalyst in vertical tubes surrounded by a cooling medium is characterized in that the catalyst tubes at their upper end are incompletely filled with catalyst and the cooling medium in fluid and/or partly vaporized form is passed over the tubes particularly approaching in height the level of the height of catalyst in the tube. (4)

R600 - Jan. 26, 1942 - Production of Diene ethers as solvents or plasticizers.

Alcohols produced either by the direct catalytic reaction of CO and H₂ on olefins containing one less carbon atom, or by the complete reduction of Oxo products are converted into ethers. (4)

R594 - Feb. 26, 1943 - Revision of R11103 IVd/12. Process for the combination of city gas manufacture and naphtha synthesis by hydrogenation of CO.

In which synthesis is accomplished by iron catalyst at pressures of about 10 - 20 atmospheres, characterized in that the direct passage of synthesis gas is employed, and in which the proportions of CO to H₂ are of the order 1: 1.8 - 2.2. (1)

R586 - Aug. 6, 1941 - Precautions or means to lessen damage to steam boilers in operation of engines.

Three claims: (a) The fuel charge pump is placed close to and, if possible, directly under the fuel storage tank and even built into this. (b) Operating in accordance with claim 1, the capacity of the fuel pump under the above conditions is determined by the vapor pressure characteristics of the fuel. (c) Claim 3, in accordance with claim 1, stipulates that the exit back pressure or pressure drop due to fuel vapor at the pump pressure side, particularly in float valves or the neck of float valve housing, is low. (4)

R584 - Oct. 8, 1941 - Process for separation of sodium soap from soap-hydrocarbon mixtures.

This is done with the help of water or alcohol diluted and distinguished in that the separation of soap as an alkali-hydroxide-free reaction mixture,

is done with an amount of water or dilute alcohol about 10 to 15 times greater than the weight of soap to be separated. Claim 2 operates in accordance with Claim 1 and specifies that the water or alcohol mixture used for soap separation has a foam suppressing substance added to it.

R578 - Sept. 8, 1942 - Processing for catalytic rearrangement of hydrocarbons, particularly aromatization, polymerization and dehydrogenation characterized in that the mixture of hydrocarbons charged to the process is freed, as far as possible, of oxygenated compounds by treating with aluminum oxide or similar metal oxides at temperatures between 150 to 400°. (1)

R569 - Aug. 5, 1942 - Production of Valuable Naphtha.

In the catalytic cracking of hydrocarbon oils in the presence of gaseous hydrocarbons with 4 to 6 carbon atoms, and preferably unbranched olefins, with attendant polymerization of the gaseous olefins, characterized in that the cracking is performed under mild conditions of about 500°, a partial pressure of the hydrocarbons about 1/10 atmosphere and residence time of 5 to 20 seconds, if necessary in the presence of water vapor, and preferably in the presence of aluminum silicate, so that only isomerization of the gaseous hydrocarbons results. (6)

R565 - Apr. 4, 1941 - Production of high octane hydrocarbon mixtures.

Cracking of higher molecular weight hydrocarbons resulting from reaction of H₂ and CO or from other sources, which are free of naphthenes, may be high in olefins and have good octane number. Hydrogenation of this naphtha lowers the octane number. The patent claims novelty in subjecting the naphtha to an aromatizing step before hydrogenation. The second claim stipulates operation according to Claim 1 and specifies treatment before aromatization with boryl phosphate, clay or other catalyst of a similar nature. (7)

R560 - Feb. 21, 1942 - Production of strong and highly active aluminum oxide-chromium oxide catalyst for dehydrogenation and/or cyclization.

Process is distinguished in that the chromium oxide or ammonia chromate is mixed with the aluminum oxide by vigorous mechanical working and with as little water as is possible, but this material when dried at about 200° and calcined at 600° results, after cooling, in the desired form. (1)

R551 - Aug. 3, 1942 - Process for catalytic splitting of hydrocarbons with the aid of reaction chambers which are alternately used in catalytic step and a decarbonization step.

Employment of activated clay, or other alumina hydrosilicates, which are regenerated after the cracking portion of the cycle by decarbonization. The heat required for cracking and the capacity for taking away the heat of combustion resulting from burning the hydrocarbon remaining on the catalyst is of almost equal proportions and is adjusted to give balance of heat requirements in the catalyst mass. (1)

R549 - Mar. 24, 1942 - Stable emulsions of hard paraffin and water used as polishing agents.

Paraffin mixture with a melting point of about 85° made by catalytic reduction of CO is emulsified by the addition of the alkali salt of carbonic acid. Free acids are made by oxidation of paraffin wax with melting points of 40 to 65° by means of chromium sulphate or nitroso-sulphuric acid. The second claim specifies that the emulsion will be freed of acids and esters which had resulted from the oxidation reaction. (6)

R540 - Oct. 17, 1940 - Catalytic cracking of hydrocarbons.

Using olefinic low boiling hydrocarbons, particularly those which are readily polymerized to high octane naphtha distinguished as follows:

Using ordinary or elevated pressure, the cracking catalyst is decolorizing clay which, if necessary, is activated with acids. The acids may be boric acid-phosphoric acid mixtures or phosphoric acid alone. Cobalt or similar salts may be used to activate the clay. (3)

R537 - Oct. 2, 1940 - Means for obtaining a desired CO-H₂ consumption ratio by control of catalyst alkalinity.

The patent claims do not appear in this portion of the reel, but the example cites the effect mentioned in the title. (3)

SECTION 2. CORRESPONDENCE ABOUT PATENTS (3)

R540 - July 11, 1941 - See Section 1 above.

R539 - June 21, 1941 - Oxidation Stable Oils.

Processing to raise the stability of synthetic oils made by condensation of olefins in the presence of aluminum chloride characterized that such lube oils are treated at about 170° with small quantities of AlCl₃ and elementary S followed by treating at about the same temperature with clay and ZnO or with MgO. The final treatment is a vacuum distillation. (3)

R538 - Mar. 31, 1943 - Sulphonation of olefin containing reaction product of CO and H₂.

Hydrogenation products are employed as charge stocks which are obtained under simultaneous addition of gases not taking part in the reaction of CO and H₂ with water gas or with gases even richer in CO and keeping the hydrogenation period on the catalyst short.

The second claim operates as in Claim 1, employing reaction product made from synthesis charge containing about equal volumes of CO and H₂, and using recycle 2.5 to 4 times the volume of fresh feed gas. (1)

R535 - Jan. 30, 1941 - Process for the production of valuable lubricants.

No patent claims appear. (1)

R630 - Apr. 28, 1943 -

The title and patent claims do not appear, but the subject seems to have been concerned with olefin synthesis and attendant oxidation of olefins. (1)

R658 - Apr. 30, 1943 - Processing for recovery of soap forming fatty acid concentrates. (1)

R618 - Apr. 2, 1943 -

No title or claims appear, but the subject matter which apparently deals with dispersion of droplets of concentrated ammonium nitrate solution on moving granular limestone appears to have been anticipated by French patent 837022 and Swiss patent 151638. (3)

R597 - Sept. 11, 1942 -

No title or claims are given, but the subject matter appears to have dealt with the production of contact mass for desulphurization of gases. (1)

R596 - June 18, 1942 -

Subject of claim not given, but appears to have dealt with oxidation of higher molecular weight aldehydes. (3)

R587 - Mar. 24, 1943 - Oxygenated Compounds.

The patent claims cover process for the production of oxygenated compounds from paraffin hydrocarbons having more than 10 carbon atoms in the molecules by treatment with nitroso sulphuric acid as well as oxygen containing gases. Small amounts of oxygen or super oxides are added before the main oxygenation step. A wide variety of inorganic and organic oxides are said to be suitable. (1)

R582 - July 10, 1942 -

Title and claim not given but subject apparently dealt with production of synthetic organic oxygen-containing compounds and separation from mixtures. (3)

R583 - Nov. 25, 1942 - Treating soaps made from free fatty acids. (4)

R565 - Nov. 25, 1941 (3) - See Section 1 above.

R564 - Dec. 14, 1942 - Production of polybasic carbon acids. (5)

R559 - Sept. 11, 1941 - Slurried Catalyst for hydrogenation of CO. (1)

R560 - Feb. 21, 1942 - (2) See Section 1 above.

R552 - Sept. 19, 1941 - Treatment of alcohol for splitting out H₂O. (2)

R557 - Aug. 14, 1942 - Production of olefin-rich hydrocarbon mixture.

The patent claim states that in the catalytic decomposition of CO and H₂ mixtures which contain olefinic hydrocarbons by means of cobalt catalysts this process is novel in that it is performed under ordinary pressure at 185-225°, using catalyst diluted with inert material and in the presence of C₂H₂. (3)

R558 - Nov. 26, 1941 - Conversion of higher alcohols or alcohol mixtures in fatty acid alkali salts.

The patent claims are partially expressed as the production of alkali salts of higher molecular weight fatty acids by heating the corresponding alcohols or alcohol mixtures with alkali hydroxide, if necessary at elevated pressure. Novelty is claimed in hydrogenation catalyst, especially metals of the iron group, the noble metals group, etc. in the presence of a small excess of alkali. (5)

R559 - Apr. 24, 1942 -

The title and claims are not given but the subject matter appears to relate to distillation. (2)

R552 - June 9, 1942 -

No title or claims are given but may have related to the reduction of alcohol and similar compounds. (3)

R547 - Sept. 19, 1941 - Recovery of pure olefins.

The patent claim is not given, but it appears that the process entailed the reduction of alcohols of known composition to form a corresponding olefin. (6)

R544 - Aug. 29, 1941 - Title and claims not stated. (1)

R545 - Dec. 18, 1941 - Olefinic fluid hydrocarbons by catalytic reaction of CO and H₂ under pressure.

Recycling a portion of the reaction product, novelty is claimed in employing a cobalt catalyst and synthesis gas having a ratio of one part CO to not more than 1.5 parts H₂, and maintaining a ratio of recycle gas and synthesis gas of about 3:1. (1)

R547 - Mar. 16, 1942 - Production of pure olefins.

See item of same number above. (3)

R544 - June 18, 1942 -

This item was mentioned above, but title and claims not revealed. The present entry is concerned with a process for the catalytic cracking, dehydrogenation or aromatization of hydrocarbons, whereby carbon deposited on the catalyst during the reaction period is removed by burning in a subsequent period. Novelty is claimed in the use of heated air passed downward through the catalyst mass, the throughput being of the order of 285 to 855 cu. meters of air per cu. meter of catalyst per hour, and the reaction period is only of such length that the amount of carbon (the film is illegible at this point). (1)

R543 - Feb. 11, 1942 - Catalytic reaction of CO and H₂ to form light hydrocarbons. (3)

R531 - July 12, 1941 -

Title and claims are incomplete, but the subject matter apparently deals with recovery of unsaturated hydrocarbons through the reaction of CO and H₂. (4)

R539 - July 29, 1941 - Further discussion and examples (2) are given for items of this same number appearing in the first part of Section 2.

R540 - Jan. 20, 1942 - (3)

Items discussed in Section 1 also.

SECTION 3. SYNTHESIS OF ALDEHYDES AND OTHER OXYGEN CONTAINING COMPOUNDS FROM CO AND H₂

This is a very generalized memorandum (8) written by Dr. Roelen of Ruhrbenzin.

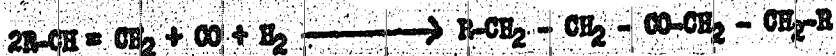
Aldehydes and other oxygenated compounds are formed in the presence of AlCl₃ by the reaction:

R-H plus CO gives R-CHO

Compounds with an olefinic double bond react:

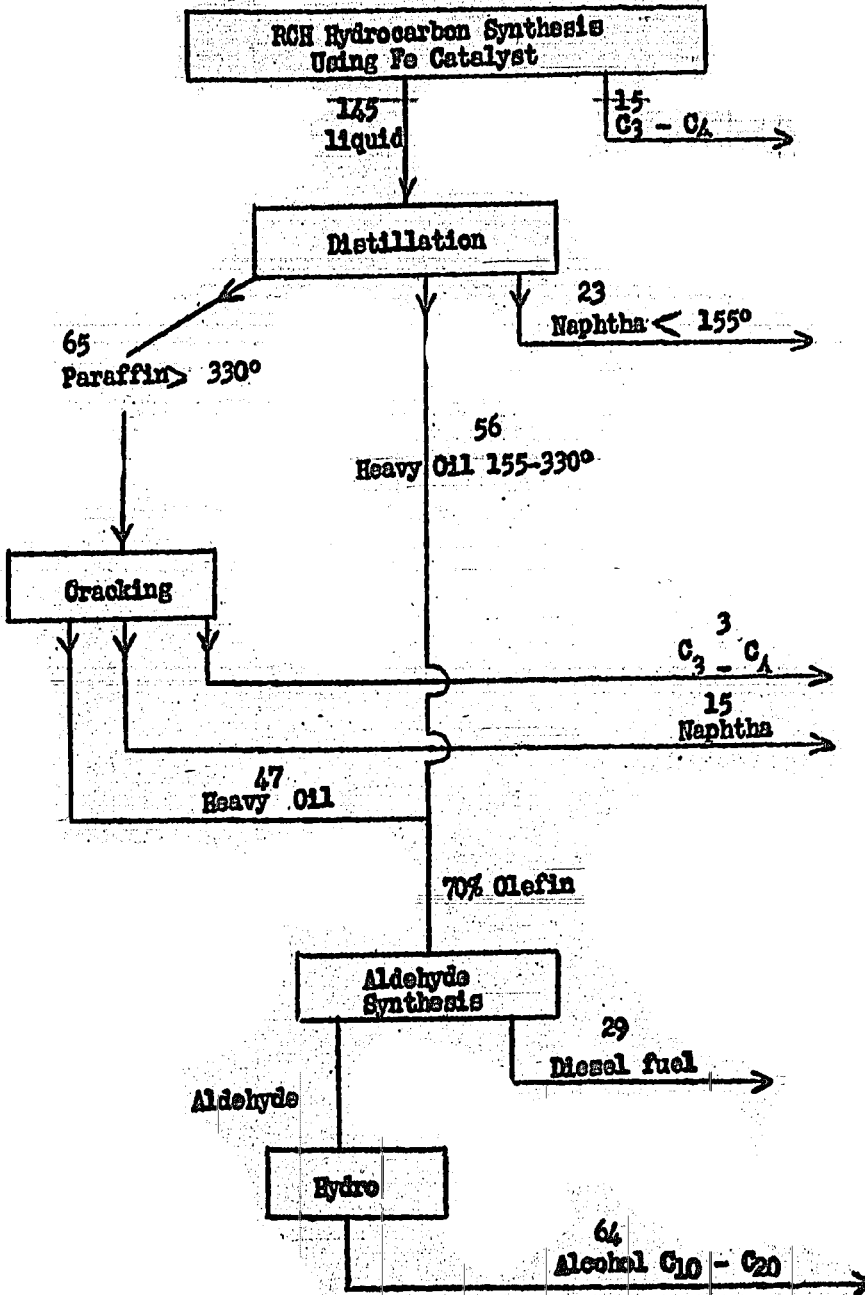


It is further found that two molecules of olefin can be converted to ketones instead of aldehydes:



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PRODUCTION OF ALIPHATIC ALCOHOLS



A wide range of olefins or unsaturated material can be employed in the above reaction.

Catalysts for these reactions include metals of the iron group (Fe, Co, Ni) particularly when used in a finely divided state. The speed of reaction increases with increase in pressure, and at 100 atmospheres, a thruput is obtained which is technically practicable.

The temperature employed covers a wide range and in general is dependent upon the activity of the catalyst and the particular charge stock being employed. If too low a temperature is used, the reaction velocity is too low. On the other hand if the temperature is too high, side reactions occur and CH_4 will be synthesized. The aldehyde synthesis from olefin, CO and H_2 is strongly exothermic. Olefins which are liquefied at reaction conditions may be slurried with the catalyst and the suspension then treated with water gas. Side reactions form such products as carbonyls. The reaction product is readily freed of dissolved metal by treating with dilute acid. Pure H_2 under the conditions for Oxo synthesis (for example 100° and 16 atmospheres with cobalt catalyst) will hydrogenate olefinic hydrocarbon and the catalysts must therefore be so chosen as to suppress olefin hydrogenation rather than reaction with CO.

Aldehyde may be readily reduced to alcohol. The synthesis of alcohol is preferably done in two steps because at such conditions in one step processing whereby CO and H_2 are combined there is very considerable hydrogenation of the olefins. The preferred route therefore is the synthesis of aldehyde from CO, H_2 and olefins in the first step and subsequent reduction to alcohols in the second.

Aldehydes are readily oxidized to fatty acids. This can be done at temperatures as low as 40° and without catalysts. Using air or oxygen, it is possible to carry on this mild oxidation reaction in the presence of hydrocarbons without decomposition of the latter.

It has been found in the synthesis process that olefin hydrocarbon in the next higher oxygen-containing homologue is produced. This brings about such an increase in boiling point that separation by distillation is simple. It is preferable to use as charge stock hydrocarbon of a given single number of carbon atoms, as for example C_6 . The users of this catalysis say they have made a complete series of aliphatic primary alcohols from C_3 to C_{20} .

Shown on the facing page is a flow diagram illustrating the products obtained by synthesis.

Memo. Mar. 5, 1940 - reporting a conference in Holten Feb. 16, 1940.

This conference held between R.C.H. and I.G. suggests early cooperation of the two concerns. It was pointed out that at medium pressure (20 atmospheres) a very wide range in olefin content of the product fraction was obtainable by using different catalysts. (Olefins derived by cracking of paraffin was practicable on a large scale. The yield of 85% approached that secured at Oppan in their cracking process. At low temperature, long-chained olefins with the double bonds at the terminal position are produced. At higher temperatures the double bond moves toward the middle of the molecule.

The Oxo process was discussed. The catalyst is the familiar Fischer type, i.e. cobalt on kieselguhr with addition of MgO. The yield of aldehyde approaches 90% at temperatures of 105-115°. The cobalt catalyst is stirred and milled with hydrogenated cetane fraction and then diluted with the corresponding olefin. It is then charged into an autoclave having a stirrer and is treated at 100 - 200 atmospheres with CO-H₂ mixtures. After a reaction period of a few hours, the CO-H₂ is released and the contents of the catalyst case are hydrogenated at 180° with pure H₂, whereby alcohols are produced. The catalyst is filtered off and again used. Experiments were in progress to substitute Fe for the Co catalysts. Koelen had made ketones from short-chained olefins whereby two molecules olefin react with one molecule of CO, for example, C₂H₄ gives diethyl ketone. Dr. Reppe mentioned his work on decomposition of unsaturated hydrocarbons with CO, as for example the reaction of C₂H₂ and CO gives acrylic acid, and from olefins are obtained the corresponding carbon acids. Apparently there was considerable interest in the large scale production of aliphatic alcohols. (5)

SECTION 4. REFINING NAPHTHA WITH ZnCl₂

This memo. Oct. 14, 1941 describes the result of treating a naphtha fraction identified as #3102. The naphtha had initial point of 60° and olefin content of 65%. It was treated with 5% solid technical grade ZnCl₂ at about 20°. The OH number was reduced from 23 to 0, whereby the alcohol in the charge was separated as double compounds of ZnCl₂ and alcohol which could be decomposed with water to ZnCl₂ and alcohol itself. The olefin content remains practically unchanged. Some work was done with concentrated chloride solution, but the proposed work covered the exploration of taking the dilute ZnCl₂ solution (see above where alcohols are separated) and reconcentrating this chemical for use as the primary agent. (4)

SECTION 5. SPECIFICATIONS FOR LIQUEFIED FUEL GAS

This material is undated and it is uncertain for whom the specifications were written. It includes vapor pressure charts for the C₂, C₃, and C₄ hydrocarbons; there is also a tabulation showing the summary of costs for bottled gas. (6)

SECTION 6. PROGRESS REPORT OF RESEARCH PROGRAM, 1944

This is a highly condensed series of monthly summaries in the period January to October addressed to Drs. Martin and Hagemann. Items mentioned in the text (26) as the subject of investigation included dechlorination of residual naphtha with mine vapor; synthesis with cracked naphtha; research on regular naphtha.

SECTION 7. AROMATIZATION OF HEPTENE AND HEPTANE

The charge stocks were either heptene derived from cracking or heptane used as standard in octane determination. The equipment was apparently a simple, electrically heated cracking furnace, and at least in the early work no catalyst was employed. Some of the experiments used a carrier gas such as H_2 , or when water vapor was employed the water gas reaction:



The heptenes were identified and concentrated as separate isomers, 1 and 2 (a, b).

The use of catalysts was rapidly developed. Supports such as activated carbon, kieselguhr, silica gel, etc. were employed. Absorption isotherms were determined for the several carrier agents. Experiments used normal butane and temperatures of 20, 100, 200, and 300°. An increase in absorption capacity was obtained by treating the carriers with hot hydrochloric acid whereby iron compounds were leached out.

The production of the catalysts is described reasonably well, and apparently covered a number of salts among which $ZnO-Cr_2O_3$ mixtures alone or on carriers showed promise.

Aromatization experiments using heptene and $ZnO-Cr_2O_3$ catalysts on various carriers were performed at about 455° and a throughput rate of approximately 0.2 volume charge per volume of catalyst per hour. (48) It was observed that heptene-1, occurring in the charge stock, is isomerized to heptene-2 or 3.

Aromatization of heptene was performed with chromium oxide catalyst without the use of carrier agents. The product contained 18% toluol. The amount of toluol in a product increases as the reaction temperature is raised and as the operating pressure is diminished. It was estimated that the same effect could be gained at 1/10 atmosphere as at 30 - 40° higher temperature and at atmospheric pressure. The yield of toluol on heptane was poor and was ascribed to the fact that equilibrium hydrogenation takes place.

The deposition of carbon on the catalyst by the cracking reaction was studied.

The incidental yield of light hydrocarbons increases from 1% to 14% as the operating temperature is increased from 350 to 480°.

The Reviewer believes that the data presented are sufficiently detailed to prove that Germany had an alternate means to hydroforming for making toluene. It was evident that the catalyst used in this early work had a strong tendency to hydrogenate, as well as to cyclize.

(This ends scanning of Reel #39)

PATENT DISCLOSURES ROYCHONDE

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