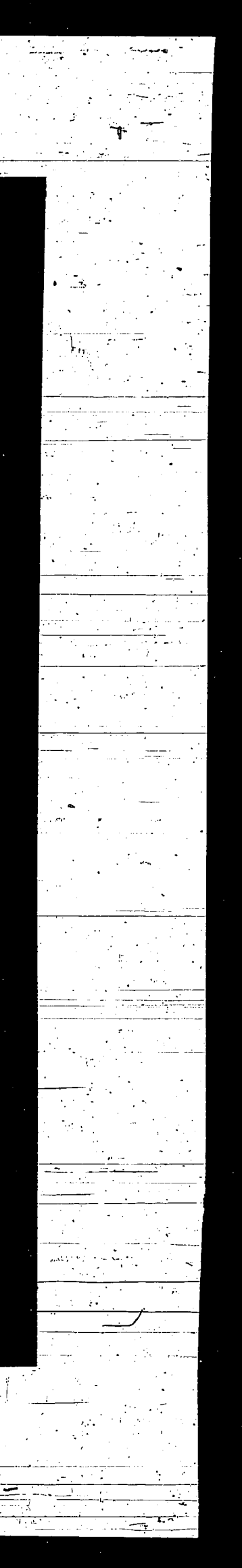


START

REEL T.O.M. 242

B.M. 29



U. S. GOVERNMENT TECHNICAL OIL MISSION

INDEXES TO MICROFILMS

INDEX - MICROFILM REEL 242
(Original designation BM-29)

	Report No.
Hydrogenation at high pressure - present status and possibility of future development. Dr. Erich Frese. 22 pages.	1
New hot separator for high pressure hydrogenation operating without deposit formation or coking. Dr. Erich Frese. 5 p. with drawings	2
Operation problems in high pressure hydrogenation. Dr. Erich Frese. 10 p.	3
Status of recent research work on hydrogenation with fixed catalyst at 700 atmospheres. Hydrogenation of Middle Oil. Dr. Erich Frese. 14 p.	4
Filtration experiments with hydrogenation residue (Abschlamm). Dr. Erich Frese. 5 p.	5
Present status of Pott-Brosche (coal extraction) Process. Dr. Erich Frese. 9 p. with drawings.	6
High pressure hydrogenation gases. Donath. 8 p.	7
Production of liquid fuels from coal, lignite, and oil shale in Europe. O. Hubmann. 111 p. and drawings.	8
Production of synthesis gas from Wyoming sub-bituminous coal. O. Hubmann. 23 p. and drawings.	9
Lurgi carbonizer with gasification of residue. O. Hubmann. 7 p.	10
Spreader for charging of Lurgi-Schweitzer retort. O. Hubmann. 1 p. and drawing.	11
Tunnel kilns for carbonization of oil shale. O. Hubmann. 12 p.	12
Lurgi Huboven for carbonization and gasification of high ash fuel. O. Hubmann. 10 p., drawing and photo.	13
Purpose and contents of short textbook on the technology of fuels. Ernst G. Graf. 18 p.	14

Index - T.O.M. Reel 242 - Continued.

	<u>Report No.</u>
Contributions to gas producer theory. Ernst G. Graf. 24 p.	15
Graphical representation of gas producer processes. Ernst G. Graf. 10 p., and drawings.	16
Gas and fuel testing methods and apparatus developed at the Institute of Technology and Fuels at Vienna. Ernst G. Graf. 5 p.	17
Coal carbonization in the laboratory. Oppelt. 16 p. and drawings.	18
Low temperature carbonization of slightly caking coals. Oppelt. 6 p., and drawings.	19
Determination of commercial yields of gas, tar, benzol and ammonia from a coal utilizing full scale coke oven. O. Hubmann. 30 p., with drawings.	20
Determination of commercial yields of gas, tar, benzol and ammonia from a coal utilizing full scale coke oven. Quantity by-products liberated during course of carbonization - second method. Oppelt. 3 p., and drawings.	21
Memorandum - Krupp-Lurgi low temperature carbonization equipment exhauster fan. 2 p., and drawings.	22
Research experiments to detoxicate illuminating gases. Ernst G. Graf. 21 p., and drawings.	23
Detoxification plant - Bohlen. O. Hubmann. 3 p., and drawings.	24
Comparison of results of oil shale carbonization in Estonia. H. A. Wahl. 4 p.	25
The Meiler-Pile carbonization system. H. A. Wahl. 54 p.	26
Information regarding refining methods of shale oil. Ernst G. Graf. 8 p.	27
Description of low temperature process for oil shale. Ernst G. Graf. 8 p., and drawings.	28
Ideas and proposals on oil shale utilization. Ernst G. Graf. 6 p.	29
Information on shale oil requested by Bureau of Ships. Karl A. Fischer. 2 p.	30
Translation Russian article: Manufacture of liquid fuels from combustible shales by method of thermal solution. M. K. D'yakova. 22 p.	31

Index - T.O.M. Reel 242 - Continued.

	<u>Report No.</u>
Carbonization of oil shale in situ. Original and translator's notes of Swedish report. 2 p., and sketch.	32
Answering of questions of Bureau of Ships regarding shale oil treatment. H. A. Wahl. 16 p.	33
Situation and prospects of development of oil shale treatment. Byron Wehm and H. A. Wahl. 78 p.	34
Generation of electric power of oil shale carbonization in Estonia. H. A. Wahl. 14 p., and drawings.	35
Oil shale carbonization plant at Kivioli, Estonia. Trockel. 5 p., and drawings.	36
Subterranean carbonization distillation and gasification of oil shale. Erick Sarapuu. 3 p., and photo.	37
Fischer assay of oil shale. Oppelt. 3 p., and drawings.	38
Comments on characteristics and refining methods of shale oils with reference to Bureau of Ships questionnaire. Oppelt. 13 p.	39
Refining of shale oil. O. Hubmann. 5 p., and drawings.	40
Advances in solvent dewaxing of mineral oils and tars - by Karl A. Fischer:	
I Introduction. 6 p.	41
II Chemical conclusions. 24 p.	42
III Crystallographic conclusions. 28 p.	43
IV Filters and phase problems. 31 p.	44
V Static charge filter cloth lab research. 24 p.	45
VI Technical viewpoints of dewaxing ideas. 29 p.	46
VII New electro-optical analysis for paraffins. 18 p.	47
Technical notes on research works of Japanese Army Fuel Research Institute. 26 p.	48

Papers on Fundamental Combustion Research
from the Institute for Liquid Fuels and Lubricants Research
at Strassburg (Evacuated to Oberlangenstadt, Bavaria)

Retake of T. O. M. 172, Frames No. 394 to 479

(1) (1)

HYDROGENATION AT HIGH PRESSURES
PRESENT STATUS OF THE PROBLEM AND POSSIBILITY OF FUTURE DEVELOPMENT

Dr. Erich Frese

INTRODUCTION

During the last few decades, the lack of native petroleum and the vital importance of this material in the national economy has led German industry to direct its efforts towards the production of synthetic oils to make up for the natural deficiency in petroleum. From a chemical point of view, petroleum and the products obtained from it are composed essentially of two elements, carbon and hydrogen. Since Germany possesses sufficient quantities of another important raw material, namely, coal (bituminous coal and lignite), whose chemical composition is closely related to that of petroleum, it is logical to consider the possibility of converting this material into vital petroleum. The fundamental difference between petroleum and coal is that petroleum products contain 2 to 3 times more chemically-bound hydrogen (in weight percent) than does coal. Consequently, it is necessary only to increase the hydrogen content of coal and to eliminate traces of oxygen to obtain products similar to natural petroleum. The process which involves the addition of hydrogen is known as hydrogenation. Two such processes were developed in Germany; both used coal as the initial raw material and resulted in the production of petroleum-like substances. These processes are:

- (1) Hydrogenation of coal at high pressures by the Bergius-I.G. Farben method.
- (2) Hydrogenation of carbon monoxide by the Fischer-Tropsch synthesis.

The first procedure, whose practical origin dates from the work of Bergius in the first and second decade of this century, was developed to its present state by the I.G. Farbenindustrie. Fundamentally, the procedure consists in introducing into the coal molecule additional hydrogen at high pressures and in the presence of suitable catalysts, thus raising the initial hydrogen content of the raw material and breaking down large molecules. By this means, the original solid material is transformed into liquid products. Simultaneously, a refining process is involved, by which harmful impurities are eliminated. In the second process, the raw materials first react with steam and oxygen to give carbon monoxide and hydrogen, which in the presence of suitable catalysts combine to produce synthetic oils. This process takes place at atmospheric or low pressure.

In Germany, the Bergius process was used chiefly for the production of aviation gasoline, automobile gasoline, Diesel oil, lubricating oil, and fuel oil for naval purposes. The higher quality gasolines were obtained from bituminous coal, and the better Diesel oils and lubricating oils, from lignite. The Fischer-Tropsch synthesis resulted chiefly in the production of high quality Diesel oils and lubricating oils, together with high-melting paraffins, which were used as raw materials in synthesizing fatty acids and as substitutes for compounds with wax-like properties. The gases which form during both these processes may further be converted into motor fuel and into synthetic high anti-knock aviation gasoline of the iso-octane type. The two procedures did not compete in Germany, but supplemented each other for the production of the necessary individual finished materials.

CURRENT METHOD OF HIGH-PRESSURE HYDROGENATION

In the following pages, the current method of hydrogenation at high pressures, as developed by I. G. Farben., will be examined briefly, and the possibility of future developments will be considered.

Description of the Process

The process is divided essentially into two parts, the so-called sump-phase and the vapor phase. In the sump phase, hydrogen is added at high pressures and in the presence of powdered catalysts to the solid or pitch-like raw materials, converting them into liquids consisting principally of middle and heavy oils. The heavy oils are recycled, for the most part, and used as pasting oils for fresh raw material; the middle oils are processed further in the vapor phase. In the vapor phase, hydrogen is used at high pressure and in the presence of a fixed catalyst bed to crack these middle oils into gasoline.

German Hydrogenation Plants

The first plant in Germany to apply this process on an industrial scale was the Ammoniakwerk Merseburg (Leunawerke) in 1927. The experience acquired there and the large quantities of experimental data obtained principally from research by I. G. Farbenindustrie, Ludwigshafen, during the next few years led to the erection of other synthetic oil plants near the source of the raw materials. These plants are listed in Table 1, together with their approximate annual production capacity. The values are given from memory and must therefore be considered only as approximate.

Table 1. German hydrogenation plants

Name of hydrogenation plant	First year of production	Types of raw material	Pressure, atmospheres		Type of finished product	Probable annual production ^{a/}
			sump phase	vapor phase		
Leunawerke (I. G. Farben.)	1927	lignite, tar from lignite, low-temperature carbonization residues	200	200	aviation, automobile gasoline, Diesel oil, lubricating oil	600,000
Brabag Boehlen	1934	tar from lignite, low-temperature carbonization residues	300	300	automobile gasoline, Diesel oil	240,000
Brabag Magdeburg	1935	"	"	"	"	220,000
Scholven	1936	bituminous coal	"	"	aviation, automobile gasoline	240,000
Ruhröl (Stinnes)	1937	bituminous coal, high-temperature pitch	700	700	aviation gasoline, fuel, coal extract	200,000
Brabag Zeitz	1939	tar from lignite, low-temperature carbonization residues	300	300	Diesel oil, lubricating oil, paraffin	280,000
Gelsenberg	"	bituminous coal	700	"	aviation, automobile gasoline	380,000
Wesseling	1941	lignite	"	"	automobile gasoline, Diesel oil	220,000

^{a/} In tons.

Table 1.- German Hydrogenation Plants (cont'd.).

Name of hydrogenation plant	First year of production	Type of raw material	Pressure, atmospheres		Type of finished product	Probable annual production ^{a/}
			sump phase	vapor phase		
Politz	1939	petroleum residues; pitch, shale oils, coal.	700	300	gasoline, Diesel oil aviation gasoline, lubricating oil, fuel	600,000
Bruck	1942	tar from lignite, low carbonization residues.	300	300	automobile gasoline, Diesel oil, aviation gasoline, fuel	1,00,000
Litzkendorf	1942	petroleum residues.	700	700	automobile gasoline, Diesel oil	50,000
Blechkammer	1944	bituminous coal, tar from low carbonization residues of bituminous coal.	700	300	automobile gasoline.	400,000
<u>Projected plants (not established)</u>						
Scholven II	--	bituminous coal.	700	700	aviation gasoline	350,000
Blechkammer II	--	bituminous coal; tar from low carbonization residues of bituminous coal.	700	700	aviation gasoline, automobile gasoline, fuel.	400,000

^{a/} In tons.

Raw Materials for High-Pressure Hydrogenation.

Bituminous coal, lignite, and the tars resulting from their high- and low-temperature carbonization, pitch, shale oil, and its residues, heavy petroleum residues, coal extract, and, in general, all bituminous and asphalt-like substances having no other specific uses, must be considered as possible raw materials for hydrogenation. Considering bituminous coals, a moderately young coal, whose ash content is not too high, is best to use. The ash content of the coal must be low, as the removal of the ash carries out of the process 2 to 3 parts of oil. At present, these oils can be recovered only at a high loss in low-temperature carbonization furnaces and with the use of a considerable amount of apparatus. Improvement of the refining process would bring about an appreciable reduction in production costs, particularly by increasing the oil yield. With this end in view, experiments involving special distillations, new methods of filtering, and improved procedures for centrifuging were under way.

Older coal, such as anthracite, cannot at present be hydrogenated. In judging the suitability of a raw material for hydrogenation, the hydrogen to carbon ratio may be taken as a rough criterion. Generally speaking, the higher the hydrogen content of the raw material, the more easily it takes up hydrogen, and, consequently, the higher the rate of conversion that may be expected in the sump phase.

Since hydrogen is to be introduced with the help of catalysts into the carbon framework, the pressure during hydrogenation is an essential factor. Leuna, the first large German plant to be installed, operated with lignite at a pressure of 200 atmospheres for both the sump phase and vapor phase. This pressure was too low for other raw materials, such as bituminous coal and pitch, and pressures were increased to 300, and later to 700 atmospheres for the sump phase. The efficiency of a

converter or yield of middle oils per cubic meter of converter space per hour, increases considerably, other conditions being the same, when the pressure is increased. The favorable effect of increased pressure is particularly noticeable in the asphalt decomposition. It has been shown experimentally that coal decomposes relatively quickly into high molecular-weight oils containing a considerable asphalt concentration, but that the decomposition of this asphalt requires a longer time. Increased pressure reduces this time interval, thus improving the efficiency of the process. For particularly resistant materials, such as bituminous coal-tar pitch from high-temperature carbonization, hydrogenation is possible only above 300 to 400 atmospheres. At present, a production of 0.250 tons middle oil per cubic meter reactor space per hour, may be considered a satisfactory output of middle oil (based on bituminous coal), for a sump phase reactor. For high-temperature pitches, the output is generally lower, and for tar oils, it is correspondingly higher.

In determining the output, an important part is played by the catalyst, small amounts of which (generally less than one percent) are added in powdered or dissolved form to the coal or paste fed into the sump-phase reactor. Generally speaking, the function of the catalyst is less important at high pressures than at low ones. Examples of liquid-phase catalysts are: Molybdenum on Fuller's earth, molybdenum on lignite low-temperature coke (grade) (R.M. 11002), basic iron hydroxide on this lignite grade (R.M. 10927)^{1/}, tin oxalate plus ammonium chloride. The molybdenum catalysts, whose use was abandoned in Germany in recent years because of the scarcity of this metal, were found to be considerably more active than the iron catalysts. The catalyst, R.M. 10927 used most

^{1/} Basic iron compounds, either of natural origin, or industrial by-products, such as "Zschimmermasse" (iron-containing discharge from the Giulini aluminum plant near Ludwigshafen), "luxmasse", or "beyermasse".

recently in almost all German hydrogenation plants was prepared at Leuna, and was composed of about 50 percent combustible material and 50 percent ash. The ash had the following composition:

Fe ₂ O ₃ , about 11 percent	CaO, about 17 percent	MgO, about 0.82 percent
SiO ₂ , about 55 percent	Al ₂ O ₃ , about 9 percent	Na ₂ O, about 0.50 percent.

Tin in acid medium proved to be a good catalyst. However, the elimination of ammonium chloride, which is highly corrosive in the presence of water, by injection of a calcium oxide suspension into the hot catchpot, impeded operation. The Scholven works used this catalyst for the hydrogenation of bituminous coal, at 300 atmospheres, whereas the neighboring works of Gelsenberg, established later, used 1.5 percent iron sulfate plus 1.5 percent "beyermasse" plus 0.3 percent sodium sulfide at a pressure of 700 atmospheres. Experiments with pitch, at the Ruhr¹ works in the presence of catalyst produced only an increase of about 15 percent in output. A certain degree of catalytic activity must therefore be attributed to the particles of ash and unreacted coal, which are almost always found in the products (25-30 percent in the heavy oil), and which, when present in sufficient concentration in the reactors, act as a catalyst. The good results obtained for experiments in which finely powdered coal was hydrogenated without addition of carrier oils, can probably be explained by the high concentration of solids and the hydrogen absorbing and transferring ability of the newly formed oils.

Problems of High-Pressure Hydrogenation.

Under certain circumstances, the nature of the ash particles present in the raw material may impede hydrogenation. Quartz particles in the presence of calcium oxide are responsible for so-called "caviar formation", which occurs mainly in reactors I and II, and which must be

removed from time to time to prevent undesirable operational disturbances.

At Leuna and Wesseling, where lignite was used as starting material, these caviar deposits constituted a serious problem. Solid particles, containing ash, deposit in the connecting lines between reactors reducing their cross section and increasing the pressure drop through the stall.

At Ruhröl, this difficulty was avoided by introducing small amounts of water in advance of the preheater (not of the heat exchanger).

Chlorine in the raw product is harmful since it reacts with ammonia evolved in the course of the process, to form ammonium chloride. The latter compound in combination with water under certain conditions is 4 to 5 times as corrosive as concentrated hydrochloric acid. This corrosive effect is noticeable on the outlet side of the stall, particularly in the heat exchangers, at points where water starts to condense (a little below 320°C.). High-pressure lines rapidly become corroded. Consequently, the chlorine content of the raw materials must be watched continually. The problem was remedied by introduction of sodium carbonate or sodium sulfide in amounts equivalent to the chlorine content. In the case of sodium sulfide, a certain amount of catalytic activity has been attributed to the hydrogen sulfide evolved in the stalls. However, experience has shown that sodium sulfide cannot be added to all raw materials, because it causes deposits in the heat exchangers and in the preheater pipes. In general, no such disturbance need be anticipated when sodium sulfide is used for coal.

For certain temperature ranges (about 280-350°C.), coal paste prepared from bituminous coal shows undesirable swelling phenomena, which affect the fluidity of the paste and are responsible for poor heat conduction. Since this condition does not occur for a composition of 40 percent coal in oil, diluting oils were frequently added at appropriate

points. In many cases, the highly concentrated paste or some portion of it was heated with traces of hydrogen in a preheater, and the use of the heat exchanger eliminated, thus making the passage through the region of swelling as rapid as possible.

Hydrogenation being an exothermic process, some means must be found to remove the heat liberated. This is most frequently accomplished either by circulating cold hydrogen or by injecting oil. The job of adding cold hydrogen is assigned to the man attending the reactors, and is done manually. If the operator fails to observe the beginning of a reaction in time, the interior of the reactor may become coked or the connecting pipes may become ruptured due to excessive temperatures. The heat release of the liquid-phase stall depends both on the material used and on the efficiency of the chamber. In general, it lies between 100 and 200 kcal./kg. of feed, giving an average value of about 150 kcal. This heat release of the liquid-phase stall is somewhat high, but it can be regulated manually by the furnace operator as needed. Should the output of the chamber be improved by introduction of a better catalyst, or by some other means, it would be necessary to remove more heat per unit volume and per unit of time. In other words, the operational procedure would become more difficult and more dangerous. It is, therefore, desirable that manual control be replaced by the automatic introduction of cold gas. Such automatic heat regulation was recently tried out in a number of stalls at Leuna and found satisfactory. The nature of the process naturally determines the limits within which the heat release can be controlled automatically. At present, we are far from having reached these limits; however, they should not be neglected in theoretical calculations for future establishments. It is true that calculations involving a 5- or 10-fold increase in the efficiency of a stall are not based on fact. At present, doubling the current output would be more than satisfactory.

For a long time, one of the principal sources of trouble in sump-phase operation was the hot catchpot. The construction of this important piece of apparatus has been the subject of much work and effort. In recent years, this problem has been solved by means of a separator whose construction has been described in another report (A New Hot Separator for High-Pressure Hydrogenation, Operating Without Deposit Formation or Coking).

COMBINATION OF SUMP- AND VAPOR-PHASE HYDROGENATION PROCESSES.

Qualifications of a Good Vapor-Phase Catalyst.

Further processing of sump-phase products is carried out in the vapor or gas phase. As already stated, the middle oil formed in the sump phase is further hydrogenated to gasoline at high pressures and in presence of specific catalysts, to give gasoline. A satisfactory vapor-phase catalyst is one that produces a good yield of high anti-knock gasoline, accompanied by a minimum of gasification. The catalyst should effectively crack large molecules and promote hydrogen saturation of the unsaturated fraction formed, without however carrying the formation of paraffin-like compounds too far. Simultaneously, the process should entail a refining procedure by which the newly formed gasoline is freed from undesirable sulfur, nitrogen, and oxygen compounds. Moreover, the activity of a good catalyst should not decrease sharply in a short period of time.

Such compounds as sulfides of the metals in the sixth group of the periodic system, particularly tungsten and molybdenum, have proved to be good splitting catalysts, but too active hydrogenation agents. Addition of chromium, nickel, cobalt, or iron in small amounts, sometimes improves the catalyst for this reaction. Addition of lead serves to limit excessive hydrogenating. The oxides and sulfides of zinc, aluminum, magnesium, silicon, calcium, and similar elements, are moderately effi-

cient splitting catalysts. Used alone at pressures of 200 to 300 atmospheres, these catalysts are not durable nor are they active in reducing phenol and pyridine groups. In consequence, mixtures of compounds from both groups were most frequently used as catalysts.

Development of Vapor-Phase Catalysts in Germany.

The progress in developing gas-phase catalysts for use in heavy German industry may be summarized briefly as follows:

The first catalyst used at Leuna consisted of about 60 percent molybdenum oxide mixed with zinc oxide and magnesium oxide. At a pressure of 200 atmospheres, the output was relatively small. After a short time, the refining action of the catalyst became insufficient. In the early 1930's, catalyst K5058, composed almost exclusively of tungsten sulfide (WS_2), was substituted. This new catalyst increased the efficiency of the stalls two to threefold even at decreased operating temperatures. In fact, everything being equal, this catalyst is the best so far developed, with respect to output. Its efficiency, refining action, and durability (one year) were all satisfactory. However, its great disadvantage was that it was too active as a hydrogenating agent, and produced a gasoline whose octane rating was poor. This difficulty was alleviated at Leuna by carrying out aromatization in some of the stalls, in presence of the catalyst first described and at high temperatures (about 550° - $570^{\circ}C.$). Gasification in these aromatization stalls amounted to 30 to 40 percent. The temperature in the 5058 stalls was maintained at 410° to $430^{\circ}C.$ Gasification in these stalls was about 15 percent. In normal times, one kilogram of tungsten catalyst cost about 12 marks. The catalyst charge for a standard stall cost about 350,000 to 400,000 marks.

The extent of the losses in the aromatizing chambers and the growing need for anti-knock gasoline led to the development of catalyst K6434, which consisted of terrana plus 10 percent tungsten. However, when used alone, this catalyst was sensitive to phenol, nitrogen compounds, and the high-boiling fractions of the middle oil (over 325°C.). As a result, it became inactive rapidly. As a consequence, the K5058 catalyst was given preference over the new one as a first-stage catalyst, but was operated at lower temperatures (about 380°-400°C.). K5058 assured the reduction of all phenols and nitrogen compounds. The middle oil was then passed over K6434, used as a second-stage catalyst, and cracked to gasoline. The gasoline had an average octane number of about 67 for middle oils from lignite, and 72 to 74 for bituminous coal middle oils.

In order to transform this gasoline into a highly aromatic aviation gasoline, a third-stage, the DHD (high-pressure dehydrogenation) was necessary. This stall was operated at low pressures (25 to 50 atmospheres) and produced 0.4 to 0.6 tons of gasoline per cubic meter of catalyst per hour. Losses through gasification ranged between 10 and 20 percent, and often higher. The catalyst was composed essentially of aluminum oxide containing 10 percent molybdic acid. The process involves the elimination of hydrogen and is endothermic, which means that the product must be heated after passing through each reactor. The last reactor is followed by a vessel containing a refining catalyst, which purifies the highly aromatic gasoline at low temperatures (about 250°C.). The DHD catalyst must be reactivated at frequent intervals by a current of air at high temperatures (about 560°C.). The octane number of the gasoline thus obtained is between 80 and 82 (motor method). With the exception of the Ruhröl works, all hydrogenation plants in Germany operated by the vapor-phase process at 300 atmospheres, and in recent years used a dehydrogenation stall for the production of aviation gasoline.

Development of Sump- and Vapor-Phase Catalyst.

It was to be expected that a process as extensive as the gas-phase process, which involved hydrogenation in one phase (K5058) and elimination of this expensive element in the next two phases (K6434 and DHD), would not be the ultimate process in hydrogenation procedure. The amount of distillation, tank space, and threefold compression, as well as the number of hydrogenation chambers, machines, and additional personnel, were considerable. Thus, it was logical to try to combine the three processes into a single operation. The Ruhröl research laboratory conducted, over a period of years, experiments whose object was to develop a gas-phase catalyst that would effectively crack large molecules, retard extensive reduction of the products to paraffins, produce little gasification, be a good refining agent, and possess durability. All the cracking catalysts prepared previously had short life, poor refining ability, and in some cases low activity under the pressure conditions used (300 atmospheres). It seemed that the desired properties could be attained only by a significant increase in the hydrogen partial pressure. Therefore, a catalyst was sought whose activity for cracking would not be affected by high pressures.

These requirements were essentially satisfied by a catalyst of type K535, whose development and applications have been discussed in another report (Status of the Recent Research Work on Hydrogenation with a Fixed Catalyst at 700 Atmospheres). The catalyst carrier was composed of 60 percent crude Fuller's earth and 40 percent activated Fuller's earth (terrana), to which was added 0.7 percent molybdenum, 2 percent chromium, 5 percent zinc, and 10 percent sulfur. The catalyst was treated with hydrofluoric acid and finally activated in a stream of hydrogen at 350°C. Preparation was simple and inexpensive.

The catalyst operated in the gas phase at a pressure of 700 atmospheres and a temperature of 490°-500°C. The gasoline output of 0.5 ton gasoline per cubic meter of catalyst volume per hour obtained for middle oil from bituminous coal is exceptionally high. The octane number (motor method) of gasoline obtained from pitch middle oil is about 82, and that obtained from bituminous coal middle oil is only slightly lower. This gasoline gives exceptionally good results in overcharged motors. In recent years, the composition of the gasoline was maintained approximately as follows: 40 to 45 percent aromatic compounds, 45 to 50 percent naphthenes, 10 to 15 percent paraffins. Slight changes in the catalyst make it possible to alter the gasoline composition. In this way, gasolines with an aromatic content of 60 to 70 percent were prepared for a time. High anti-knock gasolines were obtained from lignite or its tars. The gas fraction, approximately two-thirds of which was C₃ and C₄ hydrocarbons and the balance C₁ and C₂, represented about 16 percent of the middle oil feed.

The heat release in the reactors lies somewhere around 160 kcal./kg. pitch middle oil feed (with K6434, about 200 kcal, with K5058 according to experimental conditions, between 200 and 300 kcal.) and thus shows that the hydrogenation effect is not excessively high.

With catalysts K6434 and K5058, it was most important that the middle oil feed contain none of the fraction boiling above 325°C. because these catalysts were deactivated by carbon and asphalt deposition. With catalyst K535, however, such precautions are unnecessary. At high pressures, the catalyst is relatively resistant to high-boiling oils. In fact, it is possible not only to crack middle oil into gaso-

line, but also to split into middle oils the heavy asphalt-free oils (above 325°C.) from the sump-phase cold separator, which are normally recycled in the sump phase. The resulting output in middle oil is double that obtained in the sump phase. Even asphalt-containing pitch from low-temperature carbonization can be hydrogenated by this process.

With K5058 and K6434, the gas cycle of the liquid phase and the gas cycle of the vapor phase had to be operated entirely separately from one another. This was no longer necessary with K535. This improvement not only makes for economy in machinery and manpower, but also offers various technical advantages.

Another advantage of this process is that it eliminates the need for separate sulfurization, which is hazardous.

Yields from Ruhrol Combination Sump- and Vapor-Phase Hydrogenation Process.

The process developed at the Ruhröl was used industrially on a large scale for several years. In view of the good results obtained, the administration decided to use this catalyst in the projected plants, "Scholven II" and "Elechhammer II".

The amount of hydrogen consumed per ton of gasoline produced varied in the individual plants between 1000 and 3000 cubic meters, depending upon the raw material. Hydrogen consumption increased from tars to lignite and was highest for bituminous coal. About 6 to 10 percent of the hydrogen input was present in the end product. Most of the remaining fraction was present in the product gases. A portion was also present as dissolved hydrogen and as water, hydrogen sulfide, and ammonia. Based on the carbon content of the material to be hydrogenated, it was calculated that 94 to 98 percent conversion to liquid and gas products occurred.

One hundred kilograms of ash-free bituminous coal will yield 50 to 53 kilograms of automobile gasoline and a similar quantity of tars (100 kg.) will produce 65 to 70 kilograms.

ECONOMIC ASPECTS OF HIGH-PRESSURE HYDROGENATION IN GERMANY

The cost per kilogram of automobile gasoline in Germany varies between 15 and 25 pfennig (45-75 pf./U.S. Gallon) depending upon the plant and to some extent upon the nature of the raw material and the required processing. A raw material such as low-carbonization tar from lignite, which contains little or no ash, requires no extensive processing of the residue. As a result, the Brabag Boehlen and Brabag Magdeburg plants, in which ash-free tars were processed, were the least expensive to operate.

There are other ways in which the hydrogenation process can be made less expensive. These will be discussed below.

The coal hydrogenation plants in Germany were generally designed for a yearly output of 200,000 to 400,000 tons of gasoline per plant. The more recent plants, designed for the hydrogenation of tar, were built on a somewhat larger scale. The choice of plant size was frequently determined more by military than by economic reasons; from the military point of view, a number of small establishments was often preferable to a single large one. With a selling price of gasoline of 300 marks per ton, the yearly income at these plants, from all marketable products, was about 40 to 50 percent of the total value of the plant.

In other words, if a plant with an annual production of 350,000 tons cost about 280,000,000 marks to build, its annual income from marketable products amounted to about 115,000,000 to 140,000,000 marks.

About 25 percent of the gasoline price represented amortization costs.

An increase in the size of the plants to yearly production capacity of

2 to 3 million tons would undoubtedly make it possible to reduce the price of gasoline considerably.

Simultaneously, a considerable reduction in manpower would result. In recent years, in Germany, a plant with a yearly output of 350,000 tons maintained 5500 to 6000 people (not counting coal production). This figure, which included 40 to 50 percent women, was considerably too high and was a result of war conditions. In the writer's opinion, this figure may be reduced to about 3500 people in the existing plants under normal conditions, without endangering their operation. Under these conditions, 100 tons of gasoline would be produced per man per year. In an establishment ten times this size, it should be possible to improve this production figure three to five times or more.

The eventual improvement in the process offers another means by which it may be possible to reduce the cost of the products. It has already been stated that processing of the residues obtained by hydrogenation is both expensive and wasteful. Further experimental work in this connection would probably prove successful (see report on the "Filtration Experiments With Hydrogenation Residue", which describes the filtration of residues through porous clay filter cylinders). One method which promises good results is the processing of residues by vacuum distillation, with possible addition of superheated steam. From an economical point of view, it would be desirable to make use of the residue temperature and the converter pressure of the hydrogenation stall, and to inject the residue directly by means of automatic valves with two stages of pressure reduction into the distillation apparatus, at a temperature of 350° to 400°C, as soon as it leaves the high-pressure stall. The hydrogen dissolved in the residue, which amounts to about 50 to 60 cubic meters per ton of residue, would be liberated by the decrease in pressure and would assist the distillation by reducing the

partial pressure of the oil. The removal of the distillation residue, which contains ash, could probably be best accomplished by means of conveyers.

Another way in which the process can be improved is by introduction of gas-phase operation at 700 atmospheres, already described.

Another problem which is only partially solved is that of catalysts, especially for the sump phase. The catalysts in present use were discovered more or less empirically. Experience has shown that some catalysts are suitable for our purpose, and others unsuitable. Intensive scientific research on the subject of catalysts, based on the latest discoveries, might lead to important results. Of particular interest for this purpose would be the study of the catalyst surface by means of electron and ultramicroscopes, the use of X-ray diffraction patterns in examining crystal structure, and other similar methods. Why, for instance, is it so difficult to split asphalts that they frequently inactivate the catalyst after a short time? Are the asphalt molecules so large that they envelop the catalyst molecules, thus preventing access of other molecules to the catalytic splitting centers and rendering the catalyst inactive? If this is the case, should not catalysts be chosen with more widely spaced atom centers to give the asphalt molecules the necessary room through which to reach the centers of catalytic activity? Should we strive to develop oil-soluble catalysts of a purely organic nature (tetralin and homologues), or would an oil-soluble mixture of organic and inorganic substances be preferable? The answers to these questions will undoubtedly contribute to the elimination of the problems of hydrogenation.

A large percentage of the manpower employed at present is assigned to the supervision and accurate control of operations such as the regulation of temperature, quantity, pressure, time of reaction, and other process variables. Removal of products is generally performed

manually. Development of automatic controls, adapted to use at high pressure, would make a further reduction in manpower possible, thus rendering the process more reliable and less expensive.

Another point which deserves special attention, is the recovery of byproducts. Just as the tars derived from coal have, in the course of time, become a veritable treasure trove of valuable substances for many purposes, it seems reasonable that the oils from hydrogenation may be considered a source of valuable byproducts. For the most part, the new 700-atmosphere catalysts do not destroy the fundamental naphthenic or aromatic nature of the coal. Since the products formed are all pure, accurate fractional distillation is usually all that is needed to separate them into well-defined groups.

In this way, the crude gasoline and middle oil fraction of the sump-phase cold separator produces about 15 percent phenols and cresols, important materials in the production of synthetic resins and plastics. Toluene and other benzene homologues may also be isolated. With a suitable catalyst, the entire 150° to 200°C. fraction from the gas-phase cold separator may be recovered. Both in its chemical properties and in its specific gravity, this fraction closely resembles oil of turpentine. The need for suitable solvents in the paint and varnish industry, as well as in the entire industry of chemical solvents (waxes, polishes, shoe polishes, printing, etc.) is exceptionally great and has increased considerably in the last few years. Recent experiments in Germany, showed these hydrogenation products to be superior in many ways to turpentine oils in the manufacture of varnishes. Plasticizers, which play an important part in the varnish industry, in the production of rubber, and in many other fields, can probably be prepared by appropriate treatment of the higher fractions.

High molecular-weight organic compounds with an aromatic structure, such as pyrene, chrysene, carbazole, fluoranthene, perylene, coronene, and other substances, which can be used directly in the dye industry, or hydrogenated to compounds used for luminescent and phosphorescent purposes, can be isolated without difficulty from the hydrogenation products.

Considerable amounts of ammonia can be recovered from waste water, and considerable amounts of sulfur from waste gas. If the entire gasoline consumed by the United States were produced from coal, the nitrogen and sulfur recovered from the byproducts would probably be sufficient to meet world consumption.

Another plan which appears to offer economic possibilities is the combination of high-pressure hydrogenation with the Fischer-Tropsch process. According to this scheme, bituminous coal would be carbonized and then gasified by steam and the low-temperature carbonization tar recovered. A portion of the synthesis gas thus obtained would be used in the Fischer-Tropsch process, and the hydrogen of the remaining gas would be used in high-pressure hydrogenation of the low-temperature carbonization tars mentioned above. The calculations which would apply to such a combined process have been made by the German scientist, O. Hubmann.

CONCLUSION

It will be seen from the preceding discussion, that there exist a number of ways in which a hydrogenation plant may be improved from an economic point of view. The full importance of this procedure will become apparent during the next few decades when the natural petroleum resources begin to diminish. Coal, the present supply of which

is estimated to be sufficient for more than a thousand years, will become the chief substitute. We are squandering natural resources such as coal, of which nature has fortunately given us an abundance. Valuable substances which are present in coal and which are the result of millions of years of solar energy, are being destroyed in a few minutes by a simple process of combustion. This behavior shows a lack of responsibility towards this most precious of raw materials which is humanity's heritage. We must therefore bend all our efforts towards preserving the materials now available and towards using them as advantageously as possible. The process described above offers one means of accomplishing this aim. It is still in the early developmental stages, and a long and difficult road lies ahead of us before the problem can finally be solved. However, this should not be a deterrent. Science has solved many vital problems, to the greater good of the whole human race, and we are convinced that ultimately this path too will lead to the top of the mountain, a goal which promises to reward all our scientific and economic efforts abundantly.

Translated by
R. Brinkley

Research and Development Division
Office of Synthetic Liquid Fuels
Fuels and Explosives Division
U.S. Department of the Interior
Bureau of Mines
Central Experiment Station
Pittsburgh, Pennsylvania
2/20/47
lgf

(2) (2)

**A NEW HOT SEPARATOR FOR HIGH-PRESSURE
HYDROGENATION, OPERATING WITHOUT DEPOSIT-FORMATION OR COKING**

Dr. Erich Frese

The light hydrocarbon and gaseous products (including hydrogen participating in the reaction) resulting from the high-pressure liquid-phase hydrogenation of coal, tar, and petroleum oils are separated in the hot separator from the heavy oils, which contain unreacted material, ash, and used catalyst. In the hot separator, which is located after the last converter and is kept under the same pressure as the high-pressure converters, a level of liquid is constantly maintained in the lower section by using a differential pressure instrument that measures the liquid head in the vessel. The temperature of the liquid and gaseous products escaping in the upper part, unless additional cooling occurs is usually about 10-20° lower than the temperature of the last converter.

These hot separators, since the early development of high-pressure hydrogenation, have caused numerous disturbances by coking and accumulation of deposits mainly in the lower part. Increases in temperature and converter shut-down have resulted. Numerous improvements have been made, some of them in the construction of the separator, and others in the method of operation. The cylindrical form of the lower part of the separator was changed to conical in order to avoid deposit accumulation and to increase the velocity in the liquid region of the separator. All internal installations which favor deposits were minimized, to keep the inner segregation space completely empty. The location of the product inlet pipe was changed from center to a pocket-like introduction along the side of the separator. Another modification was the indirect cooling of the inner walls by circulating gas through spiral

pipe between the inner and outer walls, to obtain a condensation and rinsing effect at the inner walls.

Deposits in the separator could also be avoided by additional motion and stirring of the liquid. First, a mechanical stirrer was installed. But except for recently developed installations in which the agitator drive was within the high-pressure zone, the operation of a stirrer drive shaft through hot high-pressure stuffing boxes was extremely difficult and the result was a new source of continual trouble. Finally, we started to repump the hot liquid of the separator, the so-called H.O.L.D. (heavy oil let-down) or Abschläm with high-pressure reciprocating pumps. These pumps operated hydraulically using heavy oil to operate the hot valve boxes. Solid deposition was thus controlled and the liquid in the catch pot was both cooled and kept in motion.

This proved to be satisfactory, but the cost of material, machines, and labor was very high. This procedure had its own operating difficulties, especially when the separator had to be emptied for some reason and no product was available for repumping. This discussion indicates the extent of the thought and energy which was spent for years in attempting to solve this important problem of the high-pressure hydrogenation process.

In 1942 we developed at the Ruhrol, Bottrop, a separator which attained great improvement in the process in an amazingly simple manner and resulted in better operation, lower costs (especially in comparison with the repumping method), and a high degree of safety.

The method developed by us was the introduction into the lower part of the separator of a moderate amount of gas taken from the gas circulation stream which caused a whirling motion of the heavy liquid and simultaneous cooling. By this means, deposit formation and coking are avoided;

the H.O.L.D. can be taken out at a certain height above the point at which the circulating gas stream is introduced and the heavy liquid can always be kept within a certain level. It was feared that large amounts of H_2 would be carried away from the separator with the discharged H.O.L.D. Actual practice, however, showed that this was not the case.

The construction of the new separator is shown in Figure 1. In the lower part of a hot separator which was 9 m long with an inner diameter of 0.8 m (1), a distribution ring (2) was placed, through the holes of which circulation gas was introduced at the rate of 5000-6000 $m^3/hr.$ (measured by a meter). The liquid abschlamm was drawn off by the ascending pipe (3), which was surrounded by an insulating layer (4) in the form of a cone with the apex at the top. The mouth of the liquid outlet pipe was in this case about 1 meter above the gas distribution ring (2). The end of the long pipe (5) which was used to measure liquid level was approximately at the same height as the upper end of the liquid discharge pipe (3). The introduction of the product and the gas into the separator took place through the pipe (6), which was located along the wall of the separator and was bent a little at the end toward the inside, so that the incoming liquid did not run along the walls (which could cause deposition) but fell freely on the surface of the liquid within the separator. Gases escaped through the outlet pipe (7). The level of the liquid in this separator was kept 30-50 cm. below the end of the inlet pipe (6). The liquid content should be maintained in this case, at a minimum of 500-700 liters.

The principal advantages of this installation are the following:

- (1) Deposits and coking in the separator are avoided, by introducing large

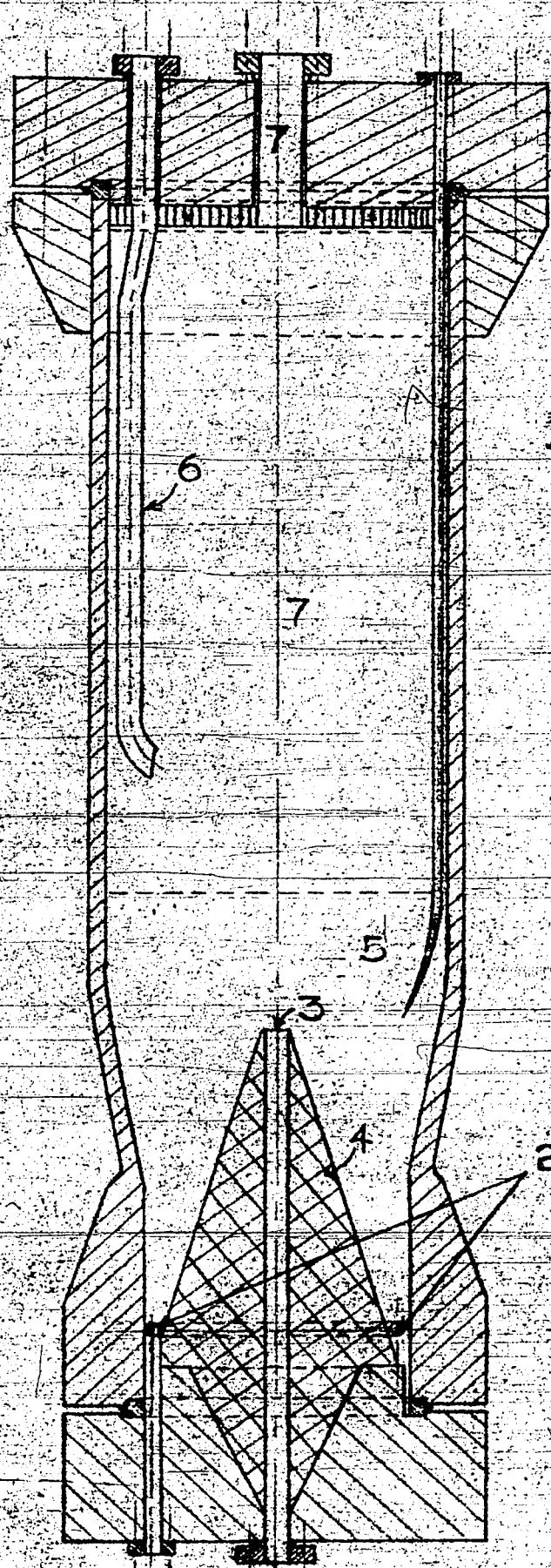


Figure 1.- Double cone bottom hot catch pot.

amounts of cold circulation gas into the lower part of the separator and inducing a whirling motion; (2) The liquid contents of the separator are cooled directly by the introduced circulating gas to 100 to 150° below the temperature of the entering material, depending on the quantity of gas and heavy liquid. By this means, a low enough temperature is reached in the separator so that temperature rise caused by any further reaction is not large enough to form coke. This construction of the separator has a special advantage should a sudden increase of temperature within the converters or an interruption of the regular product flow occur. By varying the flow of circulation gas, the separator contents can be cooled down to a low temperature, since the regular addition of heat from newly charged products is absent. Moreover, when the flow is interrupted, this separator can never be completely emptied by leakage through the valve which regulates the separator level. This is another advantage of this design, particularly when flow to the separator is resumed after a disturbance. Usually in such cases an extremely heavy abschlamm with a high content of easily settling solids is formed. The liquid in the separator dilutes this heavy material at once. The upper gaseous space of the separator is also cooled by about 10° so that a condensing and rinsing effect on the walls is assured; (3) The heat taken from the liquid by the circulation gas is added to the outlet gas which transfers it partly by way of the regenerators to the inlet products. The improvement of the heat efficiency in the chamber results in a saving of fuel gas. This point is important particularly with respect to liquid-phase chambers which operate at pressure above 400 atmospheres, because at these pressures the recovery of heat from the H.O.L.D. has not

been solved yet; (4) By taking off the lower cover, to which the liquid discharge pipe is fastened, the total separator space is readily accessible. This is not possible with the former funnel bottom separators; (5) The installation requires practically no additional labor nor expenditure of material.

The experiences of "Ruhrol" with this separator developed in their plant and used in the high-pressure hydrogenation of coal tar pitch at 700 atmospheres over a 2-year period are very satisfactory. Whereas previously, most of the shutdowns of the converters after a short operating time were caused by coking of the hot separators which were of the old type construction and which, owing to lack of space had no repumping equipment, no shutdowns of the converters have occurred with the new separators. After each shutdown of a stall (operating time up to 269 days), we found that in the separator of this new design no solid residue was formed. We can assume, therefore, an indefinite period of operation. On account of this increased onstream time, the increase in output of a sump-phase stall is about 12-15 percent at our plant.

Translated by W. Oppenheimer

October 1946

OPERATIONAL PROBLEMS OF HIGH-PRESSURE HYDROGENATION

by

Dr. Erich Fresse

3

GENERAL CONSIDERATIONS

The operation of a high-pressure hydrogenation plant is relatively hazardous, owing to the presence of high pressure and high temperature, the tendency towards deposition and plugging of the materials participating in the reaction, and the inflammability and explosive nature of the gases and liquids handled. In addition, the hydrogenation reaction is highly exothermic, necessitating extreme care in regulation of converter temperatures. Operational carelessness could cause an increase in converter temperature large enough to exceed the safe limits of operation of the unit. Continuous operation is essential for a high-pressure converter, as even a brief interruption necessitates excessive maintenance.

These characteristics of the hydrogenation process must be considered in the overall design of a high-pressure plant. In addition, all pieces of equipment, such as pumps, compressors, and circulators, must have sufficient capacity and be available in sufficient number to provide enough spares to handle any operating condition.

The smallest economically feasible plant would contain three sump-phase stalls and two vapor-phase stalls. Two of the sump-phase stalls would normally be in operation, while the third would be held in readiness as a spare. The capacity of the two vapor-phase stalls should be equal to 130 percent of the middle-oil

produced in the two sump-phase stalls. Spares for the most important injection pumps and gas compressors should be provided. Usually the spare capacity is 25 percent of the total required capacity of the injection pumps and gas compressors. In larger plants, this figure may be reduced by suitable manifolding.

For some units, particularly the circulating compressors and the paste pumps, a higher percentage of spare capacity is provided. These units are set up in sets of four as a minimum number. For example, four compressors of 10,000 cubic meters per hour capacity (3 operating, 1 spare) are installed if the plant requires 30,000 cubic meters of hydrogen per hour. If a high-pressure stall needs 30,000 kilograms feed injection per hour, the smallest number of paste presses would be four of 10,000 kilograms per hour each, with three in operation and one as a spare. For several stalls, suitable manifolding would be installed to reduce the number of spares required.

While this report does not concern itself with the quality of the materials of construction used for high-pressure installations, it may be stated that for preheater tubes and connecting piping the use of expensive alloys is cheaper in the long run than a less expensive, low-alloy steel.

COMMON OPERATING DIFFICULTIES.

The most common operating difficulties and some methods in use for their prevention are briefly summarized below.

High-Pressure Stall Equipment.

Regenerators

(Paste exchangers where incoming feed is heated by overhead gases from the hot catchpot)

The principal difficulties in these units are formation of deposits (which increase pressure drop and decrease heat transfer rates) and corrosion. The tendency to deposition is largely inherent to the nature of the materials handled. Certain types of coal tend to swell and to form a plastic mass within the temperature range of 250° and 350°C. It has also been noted that a high water content in the feed increases the tendency towards deposition and plugging. On the gas side of these units, inorganic salts such as ammonium chloride and sodium carbonate cause trouble by depositing out. Corrosion is usually found at the back end of the regenerators and is caused by ammonium chloride which is formed from the chlorine present in the charged material.

Several precautions are necessary in order to avoid these difficulties. Water content of the feed is kept at a minimum. Paste and gas must be kept in separate lines and should not be mixed below a temperature of 350°C. Distilled water is injected into the gas side in order to remove inorganic salts.

To prevent corrosion, the acid content (Cl_2) of the feed is neutralized with "Sulfigram" (Na_2S) or soda ash. As the use of Sulfigram in pitch hydrogenation has caused deposition in the regenerators, soda ash is used; but Na_2S is not injurious in coal hydrogenation.

Preheaters.

Corrosion and erosion are particularly severe in these units. At Gelsenberg, these conditions occasionally caused the hairpin tubes to burst, particularly at lower part of the bend. This difficulty can be prevented by keeping the flow velocity below 8 to 10 meters per second. The temperature of the tube wall must be very carefully controlled at a maximum of 520°C. (some plants use 560°C.) by the circulating flue gases. Temporary strengthening of the bend is not at present used as a preventative measure. Special choice of materials, continual check on the wall thickness, and a strict program of periodic exchange and testing of tubes on stream are excellent safeguards.

Converters.

Inorganic deposits ("Caviar") and coking are the most common operational difficulties. "Caviar" formation, usually most serious in the first converter, may be retarded by increasing gas velocity; if the formation is not decreased sufficiently, it must be removed by a screw-type conveyer. To minimize coking, all internal piping in the converters is reduced to a minimum. The cooling gas is now injected through the vessel wall rather than through the top head.

Increases in temperature are conducive to coke formation, and all important temperature control points are equipped with alarm devices to warn the operators of excessive temperatures. A 2°C decrease per converter from converter 1 to converter 4 favors minimum coke formation.

Connecting Piping.

Ring-like deposits are common in the hot piping between the converters. At Ruhröl, the injection of water immediately before the preheater prevents this occurrence. As previously stated, the water must be introduced after the regenerators to prevent trouble with deposition in them.

Hot Catchpot.

A large percentage of the operating difficulties in the high-pressure stall are caused by plugging of the hot catchpot. These problems are discussed in a separate report*, and a new design for this unit, which is in successful operation at the Ruhröl plant, is described.

Gas Circulation System.

Most of the operating difficulties in this section of a high-pressure hydrogenation plant are caused by plugging of lines by hydrocarbon hydrates and inorganic salts.

Hydrocarbon hydrates (usually termed "gas hydrates") can be eliminated by avoiding temperatures below 35°C. within the circulating gas system. Usually heating a small section of piping in the compressor suction line by steam tracing is sufficient to prevent low temperatures. The heat of compression is normally sufficient to protect the compressor discharge lines. Precautions are also necessary to prevent hydrate formation in the gas coolers, particularly on starting up a stall.

*"A New Hot Separator in High-Pressure Hydrogenation, Operating Without Deposit-Formation or Coking" by Dr. Erich Frese, October 1946.

Inorganic salts, particularly ammonium carbonate, can frequently be prevented from precipitating by proper heating and insulating of the lines. Depending on the feed stock, the carbon dioxide and ammonia content of the circulating gas will vary. Coal usually increases the carbon dioxide content, while coal pitch forms more ammonia. Of the two, a surplus of ammonia is more difficult to handle, as some carbon dioxide is always present in the make-up hydrogen. The formation of ammonium carbonate is more likely in the winter time.

Handling of Feed and Product.

The use of pumping tanks for providing suction head for the high-pressure paste pumps is not advisable. Careless operation may empty a tank and stop paste flow to the converters. Also, the possibility of overflowing a tank presents a serious fire hazard, particularly on account of the hot piping present. The usual procedure is to provide several circulating pumps which keep a constant fluid pressure at the suction of the paste presses. These pumps and the piping are so arranged that any excess of paste is fed to the paste presses with the surplus returning to a collecting tank in the paste preparation building. In this way, the paste press building is entirely separated from the paste preparation or storage equipment.

In operating the paste presses, all piping and particularly the pump check valves should be kept well heated. The spare pump is usually kept turning over, so that it can immediately be put into service when needed to eliminate the necessity for manipulating several heavy high-pressure valves.

Occasionally, overflow of the hot catchpot cannot be prevented, thereby permitting the heavy oil usually removed at bottom of this vessel to flow into the product separator or cold catchpot. To remove this heavy oil with its content of solid and asphaltic materials, by-pass piping is installed from the product separator to the blow-down drum. The product separator is blown down until clear of heavy oil.

An important fact in connection with high-pressure work is that valves should never be used as a positive means of separating high from low pressure systems or the high-pressure system from the atmosphere, as even multiple valves are not dependable. Suitable blind flanges should be used for this purpose.

SUGGESTIONS FOR IMPROVEMENTS IN DESIGN.

Like many other recent industrial developments, the high-pressure hydrogenation process has many possibilities for improvement.

1. Immediate improvement could be achieved by elimination of manual operation wherever possible. The regulation of hot and cold catchpot level, the rate of cooling gas injection for converter temperature control, and variations in gas circulation rates are a few of the many instances in which automatic control would greatly improve operation. The development of such instruments was in the blueprint stage at the Ammoniakwerke Merseburg (Leuna) during the war. Other high-pressure processes are automatically controlled in large industrial installations.

2. The possibility of combining liquid- and vapor-phase operation has been suggested as a means of saving heat, distillation, compression, operating, and maintenance costs. The present catalysts in general use for the vapor-phase operation (K-5058 and K-6434) are not suitable for this combined operation, as feed stocks boiling above 325°C. cause a large drop in catalyst activity and life. This fact necessitates a very careful distillation of the vapor-phase feed. Catalysts similar to K-535, developed by Ruhröl at Bottrop, can handle heavy oils without difficulty and would thus permit a combination stall.

There are, however, additional reasons for not attempting a combination of the two processes. For example, the fixed catalyst beds used in the vapor-phase require in most cases different temperatures and different gas to product ratios from liquid-phase operation. It is necessary to introduce additional circulating gas between the two operations and to regulate the temperature. This temperature control might be attained by the circulating gas addition stream, so that the combination operation is theoretically possible. However, the occurrence of normal operating difficulties, such as overflowing of the hot catchpot, would cause asphaltic materials and solids to enter the fixed catalyst bed. Installation of a second hot catchpot after the first one might prevent this difficulty.

A fixed catalyst requires a constant feed material both in quantity and quality. Attaining this would be quite difficult when directly connected to a liquid-phase stall. A small increase in temperature (even 2°C.) in the liquid-phase stall will produce

a lighter product with a larger volume. This type of fluctuation is unavoidable.

It seems possible to solve the problems incidental to this combination of liquid and gas-phase operation. However, this type of operation has thus far been limited to small pilot-plant tests. The effort is justified, but one should proceed cautiously, as additional problems will arise.

3. Another suggestion for improvement of the process is to build the liquid-phase stalls so that the converters are slightly inclined from the horizontal rather than vertical. This change will probably permit greater liquid gas interfacial area by distributing the hydrogen gas in smaller bubbles. Experimental work is needed to show whether such a construction is advantageous. New difficulties which such converters may cause are the problem of "Caviar" removal and the greatly increased area required.

4. It has been suggested that the connecting piping between converters could be minimized by stand pipes within the converters. The chief advantage is the saving of high alloyed piping material between the converters. The disadvantages are (a) reduction of the converter space which decreases output, (b) the possibility of slow corrosion and erosion of the ascending pipes, which causes short circuits, and (c) difficulty in replacing the piping. Two types of design are possible: Charging and discharging products from the top or bottom of the converter. When charging from the top, difficulty may arise when the converter is removed from service during operational emergencies, because the bottom outlet

of the converter would be used only in such emergencies and solid deposition would usually occur in this line. When charging from below, the connecting piping between the converters in the lower part of the chamber may burst if plugging occurs. This is more dangerous than the bursting of a pipe in the upper chamber. Although it is difficult to decide which operational method is preferable, we believe that the former design, that is, charging and discharging from the top may be slightly better.

Translated by
W. Oppenheimer,
November 1946.

STATUS OF THE RECENT RESEARCH WORK ON HYDROGENATION
WITH A FIXED CATALYST AT 700 ATMOSPHERES

Dr. Erich Frese

HYDROGENATION OF MIDDLE OIL

4
4

Most of the gasoline produced on a large scale in Germany during the last few years of the war came from a high-pressure process which was developed by the I. G. Farbenindustrie. This process was operated in the gas phase at approx. 200 to 300 atmospheres. In order to meet the specifications designated by the War Department, it was necessary to process the middle oil (boiling point no higher than 325°C.), which was obtained from either bituminous or brown coal, in two separate gas-phase stages. The gasoline thus produced was still not satisfactory for aviation purposes, and had to be treated in a third stage, the DHD operation (high-pressure dehydrogenation), before the required octane number was obtained.

The first stage was operated at relatively low temperature with a strong hydrogenating catalyst, such as tungsten sulfide (K5058). The reason for using this catalyst was to convert oxygen and nitrogen-constituents in the middle oil to water and ammonia. Although suppression of gasoline formation was attempted during this stage, it was not possible to prevent extensive hydrogenation of the valuable aromatic ingredients initially present in the middle oil. For the second stage a cracking catalyst such as Terrana plus 10% tungsten sulfide (K6434) was used. This catalyst converted the prehydrogenated middle oil into gasoline. High-octane aviation gasoline could not, however, be produced from the more or less paraffinic and naphthenic middle oil from the first stage. Further, the gas cycle of the liquid phase and the gas cycle of the vapor phase had to be operated entirely separately from one another, owing to the sensitivity of the catalysts, thereby necessitating additional gas circulating pumps and supervision, especially in small plants.

An additional disadvantage of the I.G. Farbenindustrie cracking catalyst (K6434) was its sensitivity to the poisoning action of oxygen- and nitrogen-containing impurities at 250-300 atmospheres. If the middle oil contained even 5% phenol, the catalyst activity decreased about 50% in a few days. At a hydrogen partial pressure of 500 or, better still, 600 atmospheres the catalyst was active in the reduction of phenols and the catalyst life was satisfactory. However, high hydrogen pressure reduced the hydrogenating ability of the catalyst to such an extent that gasolines with an unsatisfactory octane number were produced.

Owing to the difficulties encountered with gas-phase hydrogenation, Ruhröl, Bottrop, began in February 1938 to experiment with catalysts that would have both cracking and hydrogenating properties. It was desired to have durable catalysts which would reduce the oxygen- and nitrogen-containing products, and retain the fundamental aromatic character of the middle oil. We attempted from the very beginning to develop a catalyst that would produce high-quality gasoline in a single stage. After numerous tests in experimental plants, we finally succeeded in developing catalysts that produced in one stage the same high-quality gasoline as was formerly obtained in three stages. These catalysts used a partial pressure of hydrogen of 500 atmospheres and were tested in experimental units with middle oil from bituminous coal (Scholven and Gelsenberg) or pitch hydrogenation.

The disadvantage of having to use this catalyst at high pressures such as 500 to 700 atmospheres was more than compensated by the small number of high-pressure vessels and also the small distillation plant required. There were no difficulties at all in carrying out this process on a large scale. The chief advantages are enumerated as follows:

- (1) Approximately 1/3 higher yield
- (2) Smaller percentage of gasification
- (3) Smaller hydrogen requirements
- (4) Saving in construction material
- (5) One gas recycle instead of three

The low sensitivity of the catalysts towards oils of the sump phase cycle made it possible for Ruhröl to have one common gas cycle for sump and vapor phase, resulting in an additional advantage. In general, the sump phase requires a scrubbing operation of the recycle gas on account of the high hydrocarbon gas formation; the gas phase recycle gas, however, does not require such a scrubbing operation. It was now possible, by combining both sump and vapor phase recycle gas streams, to eliminate this scrubbing, as the gas phase oils acted effectively as a scrubbing medium. The cost of preparing these catalysts was low, as no large quantities of expensive metals were required. With these catalysts, it was also possible, as described later in this report, to operate economically even with asphalt-containing pitches, at essentially the same pressures. Also, it was easy to process oils distilling above 325°C. This process enabled development of fixed bed hydrogenation using materials which, until now, it was possible to split only in the sump phase.

One of the catalysts developed by Ruhröl contained a terrana-cracking catalyst. We also found that a catalyst prepared from the A.D.V. paste (Sudchemie, Munich) was well suited for this process. The paste which was mixed into the catalyst made it rigid when dry and made possible the production of cheap pellets. We found that the metals of the 6th group of the periodic system and especially molybdenum and tungsten were good hydrogenating components. The hydrogenating ability of other metals such as zinc, chromium, or iron, is insignificant by comparison. Since in Germany

only molybdenum could be readily obtained, only this component, as the sulfide prepared by thermal decomposition of ammonium sulfo-molybdate, was used.

The first satisfactory catalyst used on a large scale by Ruhröl with the middle oil from pitch hydrogenation was K157. This catalyst had the following composition: 98% cracking component (A.D.V.-paste), 2% hydrogenating component consisting of 1% molybdenum (present as sulfide from ammonium sulfo-molybdate), and 1% zinc (present as oxide).

The determination of the proper proportion of the two components was next studied. It was observed early in the study that it was necessary to vary the ratio between cracking and hydrogenating components, depending on the nature of the material being processed. Thus, a catalyst intended for use with middle oil originating from the hydrogenation of bituminous coal which contained approximately 15% phenol should possess more of the hydrogenating component; a catalyst to be used on the middle oil originating from pitch hydrogenation and containing only 3-4% of phenols should contain a smaller proportion of hydrogenating metals. However, all middle oils (from bituminous coal, brown coal, petroleum, or other sources) could be processed at 700 atmospheres in the gas phase, provided the catalyst composition was adjusted in the manner described. We worked with oils which originated from brown coal (Leuna) and from bituminous coal (Scholven, Gelsenberg, Upper Silesia). The principal aim, of course, was the further development of a catalyst for the hydrogenation of the pitch middle oil of Ruhröl. In the course of 4-1/4 years we developed 536 catalysts, which at first were tested in small 50 cc. converters; the satisfactory catalysts were later tested in 5-liter converters.

In the course of this investigation the activity of catalyst K157 was improved as far as phenol and pyridine reduction and aromatic content of the final gasoline were concerned. We also found that (1) When the

Terrana was treated with dilute hydrofluoric acid, a better cracking catalyst resulted. (The excess hydrofluoric acid was neutralized with ammonia and the resulting ammonium fluoride removed from the catalyst during the activation process.) (2) The activity of the hydrogenation component could be improved by the addition of small quantities of chromium or iron, which are only slightly active by themselves. The hydrogenation ability of the mixed catalysts was considerably better than that of the straight molybdenum catalyst.

Two catalysts (both treated with hydrofluoric acid) which we thoroughly tested on a large scale had the following composition:

K335: K157 plus approximately 2% Cr (as oxide).

K346: 60% A.D.V. paste, 40% Terrana; plus 2 g. Fe/100 g. of carrier (as oxide); plus 2 g. Cr/100 g. of carrier (as oxide); plus 1 g. Mo/100 g. of carrier (as sulfide).

Since catalyst K346 was too strongly hydrogenating, the molybdenum content was later reduced to 0.4 to 0.6%. Thus, we were able to save molybdenum, which is scarce in Germany. In the course of further experiments, we discovered that the addition of lead impeded hydrogenation, which was desirable because German requirements specified a high (over 60%) aromatic content of the gasoline. The catalysts of the type 429 and 436 all contained lead.

Catalyst K429 had the following composition:

60% A.D.V. paste, 40% Terrana, both treated with hydrofluoric acid; plus 2 g. chromium/100 g. of carrier (as oxide); plus 1 g. of lead/100 g. of carrier (as oxide); plus 0.4 g. of molybdenum/100 g. of carrier (as sulfide).

However, such a catalyst showed inferior hydrogenating ability and also poor activity for the reduction of pyridine and phenol. In addition, specifications for aviation gasoline were reduced by the German Department from 60 to 40% aromatic content. As a result, the search for more active catalysts, particularly for handling middle oils from coal, was continued.

The problem was then to make more active catalysts for phenol and pyridine elimination without entirely destroying the aromaticity of the pro-

duct. We found that the finished catalyst should not be activated in a hydrogen stream, but rather in a hydrogen sulfide stream or in a hydrogen stream which contained some hydrogen sulfide. As treatment with hydrogen sulfide is difficult and dangerous on a large scale, we added 5-10% of elemental sulfur to the catalyst. This sulfur was removed later when the catalyst was activated in the hydrogen stream at 350 to 400°C. Catalysts of this type (K534-535-536) were more active than previous catalysts and were satisfactory in pyridine reduction. At present, they constitute the best catalysts known by Ruhrol for hydrogenation at 700 atmospheres pressure. The 3 catalysts are similar in activity and composition (sulfur and molybdenum content were slightly changed), and can be adjusted to the various middle oils to be hydrogenated. If the phenol content in the middle oil was high, the molybdenum content of the catalyst was increased by 0.1%. The 3 catalysts had the following composition:

<u>Constituent</u>	<u>Catalyst Number</u>		
	<u>K534</u>	<u>K535</u>	<u>K536</u>
*A.D.V. Paste, %	60	60	60
*Terrana, %	40	40	40
Zinc (as oxide) g./100 g. carrier	5	5	5
Chromium (as oxide) g./100 g. carrier	2	2	2
Molybdenum (as sulfide) g./100 g. carrier	0.7	0.7	0.8
Sulfur (as flowers of sulfur) g./100 g. carrier (Given off as H ₂ S upon activation)	5	10	10

*Etched with hydrofluoric acid.

The following data were obtained when catalyst K535 was used:

Operating data of K535

Conv. Temp.: 500°C. at the peak of activity
 Yield: 0.5 metric tons of gasoline/m³ of cat./hr.
 Reduction of phenols: 0.1-0.2% from approx. 4.5% in feed.
 Reduction of nitrogen bases: 0.015% from approx. 2-3% feed
 Aromatic content of gasoline, approx. 45%
 Octane number of gasoline, 80-82 according to the motor method
 Octane number after the addition of 0.11% TEL, 90-92
 Heat of reaction, approx. 160 kg.cal./kg feed
 Life of the catalyst, approx. 300 days
 Gasification, approx. 15% of the A middle oil used.

The good gasoline yields obtained by Ruhröl at 700 atmos. in the gas phase operation with these new catalysts led to changes in construction plans for Scholven and Blechhammer. Further development of the high-pressure hydrogenation process will be along the lines of the advances cited above.

HYDROGENATION OF PITCH, BITUMINOUS COAL EXTRACT, AND HEAVY OILS

The cracking of the high molecular weight asphalt-containing products of the high-pressure hydrogenation of bituminous coal, high and low temperature pitch (carbonization pitch), coal extract, and heavy oil boiling above 325°C. was until now carried out in the sump phase. The powdered catalysts were mixed into a paste with the oil. The paste was then processed into heavy oil boiling above 325°C. and middle oil boiling below 325°C. The extent of middle oil production in this phase depended to a great degree on the nature of the starting product, but rarely was more than 0.25 metric tons/m³ of converter vol./hr. obtained. The catalyst was removed in the heavy oil let-down and lost.

In view of the deficiencies of this procedure, Ruhröl carried out experiments during the last few years in which hydrogenation was carried out in a fixed catalyst bed. The purpose of this research was to increase the efficiency of the process and to reduce to a minimum the quantity of residue formed. The catalysts were similar to those described in the first portion of this report. The experiments were carried out in a continuous plant using a 5-liter converter under 700 atmospheres pressure. The raw materials hydrogenated were: (1) bituminous coal tar from high-temperature carbonization (coking oven pitch), (2) bituminous coal extract (Pott-Broche), (3) heavy oil (above 325°C.) product from pitch hydrogenation, (4) bituminous coal tar pitch from low-temperature carbonization. It was found that (1) high-temperature pitch and extract could not be hydrogenated over fixed catalyst, (2) heavy oil (above 325°C.) from pitch hydrogenation and low temperature pitch could be hydrogenated.

The results of these experiments (using catalyst K534) with the raw materials 1 and 2 are summarized in a short report (TOM Reel No. 7, Bag 2732, Target 30/4.11 Bottrop 00). The activity of the catalyst in both cases decreased rapidly with time. Deposits formed on the catalyst surface increased the pressure drop through the chamber and finally necessitated shutting down the apparatus after a few days. However, we are still of the opinion that the hydrogenation of bituminous coal extract (Pott-Broche) is not an economical process when compared with coal used directly, for the following reasons: (1) high cost of production of the extract, (2) low efficiency of the hydrogenation of extract as compared with the hydrogenation of coal, (3) smaller yield of gasoline than from direct hydrogenation of the same quantity of coal.

The cold catch-pot heavy oil (boiling above 325°C.) obtained from pitch hydrogenation, which was too valuable to be used as a fuel by the Navy, was processed to middle oil (and some gasoline) in cracking experiments conducted by Ruhröl at 700 atmospheres using a fixed catalyst bed. The catalyst used was K535 (see first part of this report and particularly pp. 6,7). The yield was approximately 0.45 metric tons/m³ of catalyst volume/hr. Gasification was approximately 15 percent of the heavy oil feed with the following composition by weight of total gas product: C₁, 13 percent; C₂, 25 percent, C₃, 48 percent; iso-C₄, 2 percent; n-C₄, 12 percent. The reaction water amounted to about 3 percent of the heavy oil.

On the basis of previous experience with the cracking hydrogenation of high molecular weight oils with a low hydrogen content, as, for instance, the heavy oil from pitch liquefaction, in which the carbon content is 92.5 percent and the hydrogen only 7.5, we feared the deposition of carbon in the catalyst. We actually did find such a deposit after 62 days of operation.

This consisted of 30 percent ash and 70 percent organic material, of which 93.7 percent was carbon and 2.1 percent hydrogen. The quantity, however, was so small that a catalyst life of half a year could be predicted. The deposit was present in the form of a loose powder which did not plug the catalyst bed nor the lines and did not produce operational difficulties. During the initial period of operation, at 450°C., we found that the catalyst had a tendency to deteriorate slightly and that its activity decreased somewhat. The same phenomenon was observed in the hydrogenation of middle oil. However, the small decrease in activity could be compensated by raising the temperature to 500°C.

We specified that the catalyst should produce the greatest amount of cracking with the least amount of hydrogenation of the middle oil and that temperatures should be chosen so that the cracking stopped with the production of chiefly middle oil.

For this reason, the use of all strong hydrogenation catalysts was excluded. Pure cracking catalysts without hydrogenating metals did not prove successful, as they were poorly active and became inactive very rapidly, causing deposition on the catalyst. The most favorable results were obtained from K535 (composition given in first part of this report). The products which were formed under the experimental conditions given were approximately 39% heavy oil (B products), boiling above 330°C., which was returned to the cycle; 34% middle oil which was further processed in the gas phase to gasoline over catalyst K429; 9% gasoline; 15% gasification; 3% reaction water. The formation of gasoline was kept at a minimum. Nevertheless, even under the most favorable conditions approximately 15 to 20% hydrocarbons in the gasoline range were present in the middle oil.

We carried out experiments on the further processing of this middle oil fraction (boiling between 180 and 330°C.), under conditions similar to those described in the first part of this report. We found that for this middle oil the catalysts of the type K534 were too active and hydrogenated the gasoline too far, so that the octane number was decreased. On the other hand, pure cracking catalysts were not active enough. The best results were obtained with catalyst K429, described in the first part of this report. This catalyst contains a small quantity of lead, which controls the hydrogenating ability of the molybdenum. The aromatic content of the gasoline produced with this catalyst was almost as high as that obtained from pure cracking catalysts. As the phenol and pyridine content in this middle oil was less than 0.5% this catalyst could satisfactorily effect its reduction. Remarkable in this connection was the comparative ease of cracking this middle oil. In spite of fairly low temperature in the converter (approximately 475°C.) the gasoline yield using catalyst K429 with this oil was approximately 0.8 metric tons/m³ of cat./hr. The octane number of the final gasoline (motor method) was nearly 81, and with 0.12 vol. percent TEL, approximately 91. The content of aromatic hydrocarbons was approximately 40%. The gasoline was very similar to the D.H.D. gasoline made in Germany according to aviation gasoline specifications.

In the cracking hydrogenation of heavy oil to middle oil over fixed catalyst beds we are primarily concerned with a combination of liquid and gas phase hydrogenation. Part of the oil was probably present in the reaction space in the vapor phase, whereas a larger part of the oil was probably present as a liquid and thus passed over the catalyst. Since the reaction product even at room temperature was liquid and free of solid materials, one would think a hot catch-pot unnecessary. Neverthe-

less such a hot catch-pot is necessary for the following reasons. In the feed there are present high molecular weight, high-melting organic compounds that were not converted in the sump phase. On account of the ease with which the heavy oil dissolves substances of aromatic character, these compounds are mostly present in dissolved form. It was found that even with the use of a fixed catalyst bed, the greater portion of these compounds was not changed. As the reaction product became richer in hydrogen than the starting material, it dissolved these substances less easily; on cooling even only slightly all of this material precipitated out in big flakes or crystals. In no case was the crystalline precipitate more than 1.5% of the total reaction product. Generally, it was only about 0.5 to 1%. But on account of their great volume and gum-like character, these compounds caused frequent disturbances in the operation by plugging up the cooler and the lines of the liquid level measure apparatus of the cold catch-pot and therefore had to be removed before the material was cooled. The apparatus was therefore modified in such a fashion that the reaction product went directly from the converter to a hot catch-pot, as was the case in the old sump phase operation. In this hot catch-pot kept at 350°C., the heaviest oils condensed together with the high-molecular weight crystalline material, the latter remaining in solution at that temperature. The lighter products passed from the hot catch-pot to the cooler and separator. The products from hot and cold catch-pots were then combined.

After some time, a precipitate formed again at the bottom of the container, so that it was possible to decant from the top clear reaction product for distillation. The thick paste-like residue was centrifuged

and the filtrate further processed with no difficulty. The organic analysis of the crystalline compounds obtained from the residue showed a high percentage of a compound identified as coronene, $C_{24}H_{12}$.

E. Clar [Z., II2730 (1931)] in 1931 unsuccessfully attempted the synthesis of the hydrocarbon. The first successful synthesis was reported in 1932 by R. Scholl and K. Meyer [Ber., 65, 902 (1932)], who reported coronene as a substance melting at 429-430°C., crystallizing in yellow needles, and giving a blue violet fluorescence in organic solvents. A few years later, the I. G. took out several foreign patents which described the production of coronene in conjunction with some other polynuclear aromatic compounds such as carbazole, pyrene and their homologues, hydro-pyrene and benzoperylene, from the residue of cracking hydrogenation. In British patent 816,162, (1937) coronene is described as melting at 430-432°C. and having a bluish fluorescence in organic solvents. In 1940, M. S. Newman described the synthesis of hexabenzobenzene (coronene) [J. Am. Chem. Soc., 62, 1687 (1940)] with a m. p. 437-440°C.; the material crystallized in yellow needles. The coronene produced by Ruhrl crystallized in light yellow needles melting at 428°C. The chemical elementary analysis and the molecular weight agree with the values calculated.

Only 2 patents refer to the uses of coronene. An I. G. patent describes the phosphorescent materials produced by coronene in combination with perhydroanthracene or pyrene. The General Aniline and Film Co. mentions production of sulfur dyes from coronene and sulfur or sulfur-containing materials. It should be remembered, however, that coronene was very scarce. Previous to its discovery by the I. G. in the hydrogenation and cracking residues, the cost of coronene in Germany was, according to R. Scholl and K. Meyer [Ber., 71, 467 (1938)], 1000 Marks per gram. It was, however, in connection with the production of middle oil and gaso-

line from either the heavy oil from bituminous coal tar or bituminous coal hydrogenation that pure coronene could be obtained in large quantities as a by-product. This, also opens up the possibilities of further technical use of coronene in the near future.

Experiments were carried out by Ruhrol["] on the hydrogenation of bituminous coal carbonization/^{tar}pitch over fixed catalyst beds at pressures of 700 atmospheres. These experiments are described in a comprehensive report by TOM Reel 7, Bag 2732, Target 30/4.11 Bottrop YY. The following information was obtained: (1) Carbonization pitch can not be hydrogenated in the sump phase at 700 atmospheres as deposits formed in the converters after a short time and prohibited further processing; (2) Carbonization pitch may be hydrogenated with good results under certain conditions over a fixed catalyst bed (K535) at 700 atmospheres, without the formation of deposits. From 100 parts of carbonization pitch approximately 85% of hydrogenated oils, 10% gasification, and 5% water were obtained; (3) The special conditions included a thermal pretreatment of the pitch with subsequent filtration over Kurtzen filters; (4) The middle oil which was produced under Item (2) may be processed in the gas phase over a fixed catalyst at 700 atmospheres to a high quality gasoline. The significance of these experiments is that it is possible to hydrogenate products which contain large quantities of asphalt, using fixed catalyst beds in continuous operation.

Preparation of the Ruhrol Gas Phase Catalyst K535

Materials required for preparation of 60 kg. of finished catalyst are: 90 kg. A.D.V. paste with an average water content of approximately 60%, 24 kg. of Terrana, 4.1 kg. of hydrofluoric acid (70-72%), 3.0 kg. zinc oxide (ZnO), 6 kg. sulfur (as flowers of sulfur), 2.3 kg. of chromic acid anhydride (Cr₂O₃), 1.35 kg. of ammonium sulfo molybdate (NH₄)₂MoS₄.

17 kg. of ammonia density 0.910.

Approximately 90 kg. of A.D.V. paste were mixed in a mixer during the addition of 0.1 kg. of hydrofluoric acid over a period of 1/2 hr. After 10 kg. Terrana were added, the mixture was agitated for another 10 minutes. After the addition of 3.0 kg. zinc oxide and 2.3 kg. of chromic acid anhydride (as a 50% solution) the mixture was kneaded for another 10 minutes until homogeneous. Then a further quantity of 10 kg. of Terrana was added and the acid mixture neutralized with approximately 8 kg. of technical ammonia, 25% solution. After that, another 10 minutes' kneading followed. Then 6 kg. of sulfur as flowers of sulfur were added and kneading continued for 10 minutes. Finally, the prescribed quantity of 1.35 kg. of ammonium sulfo molybdate, dissolved in 9 kg. of 25% ammonia, and the remaining 4 kg. of Terrana were added. Kneading of the mixture was continued for approximately 20 minutes longer. The paste thus formed was compressed into one large cylinder and then manufactured into small cylinders approximately 10 mm. in diameter by pressing the material through a vertical extruder. The granules were dried at 70-75°C. for 3 or 4 days. Finally, the pellets were activated in a hydrogen stream at 350-360°C. for 12 hours.

Translated by M. Leva
November 1946

FILTRATION EXPERIMENTS WITH HYDROGENATION
RESIDUE (ABSCHLAMM)

Dr. Erich Frese

5

According to the process used by I. G. Farbenindustrie, the unreacted solid components and the ash from the raw materials, coal, lignite, pitch, heavy residual oils, etc., are removed in the so-called hot separator of the high-pressure plant, together with heavy oils, as heavy oil let-down or abschlamm (H.O.L.D.). The concentration of solid material in this slurry should not be permitted to rise above 30 percent; the oil content is at least 70 percent.

It is necessary for the economy of this process to recover for recirculation as great a portion of the heavy oil as possible. In working up this H.O.L.D. an oil, obtained during hydrogenation, was first added so that the solid content was reduced to 15 percent; the solids were then partially separated in "Laval" centrifuges. That portion containing about 8-10 percent solids and constituting about 75 percent of the total oil fed to the centrifuges, was used for repasting the coal; the portion with a solids content of 35 to 38 percent, containing the remaining 25 percent of the total oil, was treated at about 530°C. with small amounts of steam in low-temperature carbonizing furnaces (Krupp ball furnaces with conveyors). The carbonization oils were used in the oil circulation of the hydrogenation process: The lighter fraction was used as A-middle oil feed to the gas phase, the heavy oil for pasting fresh coal.

The use of this process is relatively costly, inasmuch as it requires expensive and extensive equipment and results in high losses of

oil, especially during the carbonization; therefore, experiments were started at I. G. Farbenindustrie to solve this separation problem by another method such as filtration. However, satisfactory results were not obtained, because the asphalts in the residue rapidly clogged the filter cloth. Addition of diluents, washing of the filters by thin oils, and similar manipulations were unsuccessful in overcoming this difficulty.

Finally, we (Ruhröl) tried to solve the filtering problem by the use of filter cylinders of ceramic material, as the Ruhröl G.m.b.H., Bottrop, obtained satisfactory filtrations in the coal-extraction process (Pott-Broche). Using the same ceramic material, experiments were run on a small laboratory scale with the residue from pitch hydrogenation with promising results. Transition to large-scale operation was planned.

The results of the laboratory filtering tests showed that when the residue was diluted by about double its volume of A-middle oil from the sumpf-phase, it could be filtered one third as quickly as coal-extract effluent. With diluted pitch hydrogenation residue we obtained a mean product rate of $200 \text{ l./m}^2 \text{ filter surface/hr.}$, while in the large-scale operation with coal extract, filter product rates of $700-500 \text{ l./m}^2 \text{ filter surface/hr.}$ or an average of $600 \text{ l./m}^2 \text{ filter surface/hr.}$ were obtained.

We can therefore calculate a throughput of about 4.2 m^3 of diluted oil/cylinder/hr., i. e. about 1.4 m^3 of non-diluted residue, as the filter cylinders used by Ruhröl have a filtering surface of 21 m^2 each. The daily performance of such a filter would be about 34 m^3 of undiluted residue.

This performance is, of course, still unsatisfactory. However, I believe that we may expect an increase in filter performance by continuing the experiments with additions of small amounts of "Bleicherde."

flowers of sulfur, H_2SO_4 , or other ingredients.

As our filtering tests were carried out with a residue from pitch hydrogenation, further experiments should determine whether this method is also applicable to the residue from coal hydrogenation. We believe that better results would be obtained as the coal hydrogenation residue contains a larger porous ash skeleton and less asphalt.

On a large scale with hydrogenation residue, the procedure would be as follows: About 33 percent of the residue are mixed thoroughly by stirring and repumping with about 66 percent A-middle oil from the liquid phase boiling between 180-320°C., or better still with a light fraction of this oil boiling between 180-230°, then heated to 150°C., filtered on filter cylinders of ceramic sintered material of a definite grain size, and washed well with the same middle oil or the light fraction that is used as diluent.

The filtrate is separated in one distillation into middle and heavy oil. The middle oil is used as diluent for additional residue; the heavy oil is used as pasting oil for coal or other raw material. The washed filtration residue, which still contains 25-30 percent oil, is removed from the filter and steam distilled in a rotating vessel at about 360°C. All except 0.5 percent of the oil is recovered. The oil is used as dilution oil.

A short description of the filter cylinder appears on the next page.

The selection of diluting oils that can dissolve asphalts and contain sizable amounts of phenols or their homologues, seems to be important. Precipitation of asphalts in the residue and consequently poor filtration occurs when paraffinic oils are used as diluents. The A-middle oils of the sump-phase hydrogenation of pitch and bituminous

coal, which are readily available, can be regarded as usable oils.

The advantage of the filtering process over the low-temperature carbonization is the low oil loss, which is about 25 percent in carbonization and below 8 percent of the undiluted residue oil in the filtering process. The gain, therefore, of recharged oil would be 40 m^3 daily in each operating coal chamber with an hourly injection of 32 m^3 coal paste and an hourly H.O.L.D. of 15 m^3 . If we assume a 60 percent gasoline yield from this oil, it would mean that 7 percent more gasoline could be produced from 100 parts of coal.

Description of the Filter Cylinders and Their Operation

Description. The filter cylinders used at Ruhröl were made of sintered quartz-chamotte material of a certain grain size purchased from Schuhmacher in Bietigheim, Württemberg. Rings of this porous filter material were cemented together by "Klingerit" packing rings soaked in water-glass and formed into hollow cylinders arranged vertically within a pressure vessel, 32 cylinders in each pressure vessel. The total filtering surface of one cylinder was 21 m^2 .

At the lower end of the filtering vessel was a conical funnel with an automatic patented closure through which the filter cake was dropped into a container; on the bottom of this vessel was a contrivance with rotating scrapers to disintegrate the cake. A "Redler" conveyor under the container carried the filter residues to the rotating vessel in which the steam distillation mentioned above was carried out. The whole installation was blanketed by carbon dioxide.

Operation. The hydrogenation residue+diluent mixture, heated to 150°C ., is fed by steam-operated piston pumps into the filtering plant. In

the pressure vessel the filtrate passes through the cylinders from the outside inward and runs off at the lower ends into a common pipe, leaving filter residus deposited on the outside of the cylinders. The pressure during filtration is kept at 4-5 atmospheres. After the residus has reached a certain thickness, the liquid contents of the filter vessel are blown back into the raw material container by means of CO₂ pressure. The filter cake is then ready for washing. The filter vessel is now filled with solvent, which removes all the heavy oil from the filter cake.

After removing the solvent from the pressure vessel, the filter cake is dried by hot CO₂ for a short time. Then the conical filter closure is opened and the filter cake accumulated on the outside of the cylinders is thrown into the collecting vessel by suddenly blowing CO₂ at 8 atmospheres pressure into the inside of the cylindrical filters. The excess CO₂ can escape through a suitable separating vessel which removes any entrained oil. The scraper device on the bottom of the collecting vessel pushes the residue through an opening onto the "Redler" belt, which carries it to the rotating steam-distillation vessel.

The hourly performance of such a filter in large-scale operation with decomposed coal extract was about 12-15 m³. The number of hourly filtrations was about 3-4. In such a filter up to 5000 filtrations have been carried out until the single rings had to be renewed. Regeneration of the filter rings is not economical.

Translated by W. Oppenheimer

October 1946

6

6

PRESENT STATUS OF THE POTT-BROCHE (COAL EXTRACTION) PROCESS

Dr. Erich Freese

INTRODUCTORY REMARKS

The possibility of extracting coal by various solvents has long been known. The early experiments were run under mild conditions and were chiefly concerned with obtaining a general knowledge of the chemical structure of coal. In order to obtain better yields, increased temperatures and pressures were used. Under such conditions extensive changes in the coal structure by depolymerization could not be prevented.

At present it is possible to dissolve most of the organic material in coal at pressures above 100 atmospheres and temperatures above 400°C., using suitable solvents, such as tetralin, tetralin-cresol, and middle oils resulting from coal or pitch hydrogenation. After filtration a substantially ash-free extract is obtained. Attempts to produce liquid products from this extract by high-pressure hydrogenation have been unsatisfactory. The yields are much smaller than those obtained from the hydrogenation of coal itself. Moreover, as only 75 to 80 percent of the coal is present in the extract, the production of gasoline from coal by direct hydrogenation is much more efficient than by extraction. In addition, the cost of the extract is relatively high. For these reasons, the extract produced in recent years by the Ruhröl, Bottrop, was converted to coke, which was processed into ash-free electrodes for the production of aluminum and electro-steel. The coke was exceptionally well suited for this purpose.

The early coal extraction work at Ruhröl was performed with a solvent composed of 80 parts of tetralin and 20 of cresol. Approximately 20 percent of the tetralin was converted to naphthalene during the extraction process and was regenerated by hydrogenation. Solvent losses, which had to be compensated by the introduction of fresh tetralin, were so high that the process was not economical. As a consequence, tetralin was replaced by middle oils resulting from high-pressure hydrogenation. These experiments gave good results under certain conditions, and, for this reason, the plant was modified to permit the use of pitch hydrogenation middle oil. Figure 1 represents the flowsheet of the Pott-Broche extraction process used by Ruhröl, Bottrop.

The following pages present a summary of the coal extraction work carried out in the laboratory of Ruhröl during recent years. The progress of the work on the solvation process is also reported.

EXPERIMENTS WITH PULVERIZED COAL (DRIED) FROM THE MATHIAS-STINNES MINE

The Use of A-Middle Oil as Solvent

This coal was extracted by A-middle oil (boiling range 200-315°C.) from the hydrogenation of pitch (see Figure 1). Optimum results, that is, a yield of about 80 percent of extract, based on the coal, were obtained under the following conditions:

1. Extraction temperature was 400°C., using fresh A-middle oil, and 395°C. with used and blended solvent.
2. Reaction time was 90 minutes. A shorter reaction time necessitated the use of increased reaction temperature.
3. Coal content was 33-1/3 percent. Higher coal content caused operational difficulties.

4. Recycle ratio was 60-55 percent used solvent to a minimum of 40-45 percent fresh A-middle oil before each recycle period. Lower concentrations of fresh oil caused a rapid decrease in the extraction yields, because an insufficient quantity of hydrogen-donor (tetralin-like) material was present. Addition of small amounts of hydrogen in laboratory experiments increased the permissible content of recycle middle oil to 75 percent, thus requiring a make-up of only 25 percent fresh A-middle oil. In large-scale tests with hydrogen, serious coking difficulty caused by the accumulation of material in balls the size of pigeon eggs in the ascending pipes necessitated shut-down of the plant after only brief operating periods.

Discussion of Gaseous and Liquid Products
(so-called "Coal Oils")

1. Partial splitting of the coal produced low-boiling gasoline-like products, or "coal oils", to the extent of about one percent of the coal charge.
2. The coal oils which are within the boiling range of the solvent, middle oil, could not be isolated. However, it is believed that the decreased efficiency of the recycle solvent for the extraction process was caused by the formation of coal oils, and the resulting decrease in tetralin-type compounds in the solvent.
3. The formation of coal oil was dependent only on the reaction temperature. Addition of hydrogen during the reaction was without effect.
4. The high-boiling or resin-like oils formed during extraction were found in the high-boiling fraction of the distillate or remained as residue in the extract, depending on the melting point of

the extract produced. With an extract of 230°C. melting point, material balances showed no loss in quantity of material, but in quality. To obtain this melting point, distillation of the ash-free filtrate resulted in a replacement of the losses of middle oil solvent by newly formed higher-boiling oils originating from the coal.

5. Gasification amounted to 2 to 3 percent of the coal feed and 0.2 to 0.3 percent of the solvent. Extent of gasification was a function of the reaction temperature and reaction time and independent of the amount of hydrogen added.

Influence of the Nature of the Solvent

Experimental work showed that the middle oil boiling between 200° and 315°C. was a very suitable solvent. Higher-boiling oil fractions gave satisfactory yields of extract and stable filtrates. However, the raw extract proved so difficult to filter that the use of these high-boiling oils was out of the question. The addition of hydrogen did not improve the filterability.

Unsatisfactory results were obtained with B-middle oil from vapor-phase hydrogenation, with the middle oil produced by hydrogenation of the sump-phase cold separator residue over a fixed catalyst (see report on "Status of the Recent Research Work on Hydrogenation with a Fixed Catalyst at 700 Atmospheres"), and with the middle oil from the cold separator when hydrogenating carbonization pitch over a fixed catalyst (see same report). The reason for poor results with these oils may be that these oils were too naphthenic in nature and were too highly hydrogenated (hydrogen content, 9.5-9.8 percent).

Extensive experiments were performed with middle oils obtained in sump-phase hydrogenation at the Gelsenberg and Scholven

plants. The middle oils obtained in 1940 were unsatisfactory as solvents. However, when about one percent of hydrogen (on the basis of coal feed) was added, filterable extract yields of 83 to 85 percent were obtained. These results were reproduced in several series of experiments in which recycle solvent was blended with 40 to 50 percent of fresh middle oil and hydrogen added. The extract yield averaged about 80 percent.

Later experiments with middle oils produced in 1942 from the same plants gave less satisfactory results, even with the addition of hydrogen. These oils were poorer in hydrogen than the 1940 oils. Improvement in extract yields resulted when the extraction temperature was lowered to 380°C., but was accompanied by filtering difficulties. This problem was solved by rapidly raising the temperature to 400°C. for a short interval after the extraction period.

EXPERIMENTS WITH GELSENBERG COAL

Gelsenberg coal, which is geologically younger than Mathias-Stinnes coal and quite different structurally, could be extracted with middle oil resulting from hydrogenation of Ruhröl coal separator pitch. However, reaction could be obtained only by adding hydrogen. Mathias-Stinnes coal could be extracted with middle oil from sump-phase hydrogenation at Gelsenberg, when hydrogen was added and reaction was performed for 60 minutes at 380°C., followed by short after-treatment at 400°C. No satisfactory yields were obtained, however, from the extraction of Gelsenberg coal with Gelsenberg middle oil. As other experiments showed that younger bituminous coal can be extracted as successfully as the Mathias-Stinnes coal, the poor results obtained

with Gelsenberg coal may be explained by its specific structure, which makes extraction with solvents difficult. In addition, the Gelsenberg middle oil is an inefficient solvent, so that the net result of extracting Gelsenberg coal with Gelsenberg middle oil was highly unsatisfactory.

DESCRIPTION OF LARGE-SCALE OPERATION

Operating Conditions and Yield

In large-scale extraction of bituminous coal, only Mathias-Stinnes coal was used. The slurry was composed of one-third coal and two-thirds A-middle oil from the hydrogenation of pitch. Contact time in the reaction chamber was 60 to 90 minutes. Temperatures were generally higher than those used in laboratory experiments; namely, 415 to 430°C., with the higher temperature at the inlet of the reactor. The pressure was kept at 100 atmospheres in the reaction chamber. The extract yield was usually 78 to 84 percent, based on ash-free coal. When the crude extract did not filter properly, it was run through the reaction chamber a second time. This procedure was usually successful.

The addition of hydrogen was unsuccessful on a large scale. Within a very short time, ball-shaped plugs appeared in the ascending pipes. However, during normal operation without hydrogen deposits gradually formed on the walls of the hair-pin tubes, particularly towards the end and in the ascending pipe. Operating periods as long as 100 days were achieved. The tubes were then removed for cleaning and replaced by spare tubes. Velocities in the ascending tubes were 15 to 20 cm. per second, and in the descending pipe, 30 to 35 cm. per second. It was assumed that under these operating conditions no noticeable quantities of gas other than dissolved gases were present in the apparatus.

From 100 parts of coal (moisture- and ash-free basis) were obtained:

extract.....	68-70 parts	
gas containing about 70 percent paraffin hydrocarbons.....	3	"
gasoline.....	1	"
residue containing 25-30 percent ash.....	26-28	"

Operational Details

In the drying and grinding plant (producing 5.5 to 6.0 tons per hour of dry, powdered coal and marked St-10 on the flow diagram), coal was dried and pulverized until 60 to 70 percent of the material was smaller than 0.06 mm. The pulverized coal was made into a slurry with 2 parts of solvent to 1 part of coal. The solvent contained material from the tank St-23 and wash filtrate from St-13 (see filter washing discussion below). The slurry was heated to 80°C. and then fed by means of piston pumps into high-pressure paste pumps by which the coal-solvent mixture is injected through the reaction chamber, St-12, at a rate of 15 to 17 tons per hour. Extraction and solution of the coal occurred at a temperature of 415° to 430°C., pressure of 100-150 atmospheres, and contact time of about one hour.

The reaction chamber was similar to the preheater of a hydrogenation stall and consisted of a system of pipes, 15 meters in length, connected in series. The descending pipes had an inside diameter of 120 mm., the ascending pipes, 180 mm. The crude extract was cooled, released from pressure, and passed at a temperature of 150°C. to the filtration unit, St-13. Filtration separated the crude extract into a residue consisting of ash and unreacted coal, and an

ash- and solid-free filtrate. The latter was pumped to the distilling unit, St-15, for further processing.

Each filter unit contained 32 "Kerzen" filters (see report on "Filtration Experiments with Hydrogenation Residue"). These were rings of special porous clay filter material cemented together by "Klingerit" packing rings soaked in water-glass and formed into hollow cylinders arranged within a pressure vessel. The total filtering surface of one cylinder was 21 square meters.

The average throughput per filter unit was about 13 tons of extract-solvent-residue mixture per hour, corresponding to about 3.2 tons extract per filter unit per hour or 0.610 tons filter feed per square meter of filtering surface per hour. The filter pressure drop was 3 to 4 atmospheres and the filter temperature, 150°C. The filter cake or residue was washed with solvent at the same temperature and pressure. The first small portion of the wash solvent was added to the filtrate, the remainder returned to be used in making up the coal-solvent slurry.

The unreacted coal and ash residue, after removal from the filter units, was carried by a "Redler" conveyor to St-13a for recovery of the wash solvent. The residue was freed of oil in rotating drums at a temperature of about 360°C. The residue from this operation, containing 25 to 30 percent ash and less than 0.5 percent solvent, was used as fuel in the boiler house.

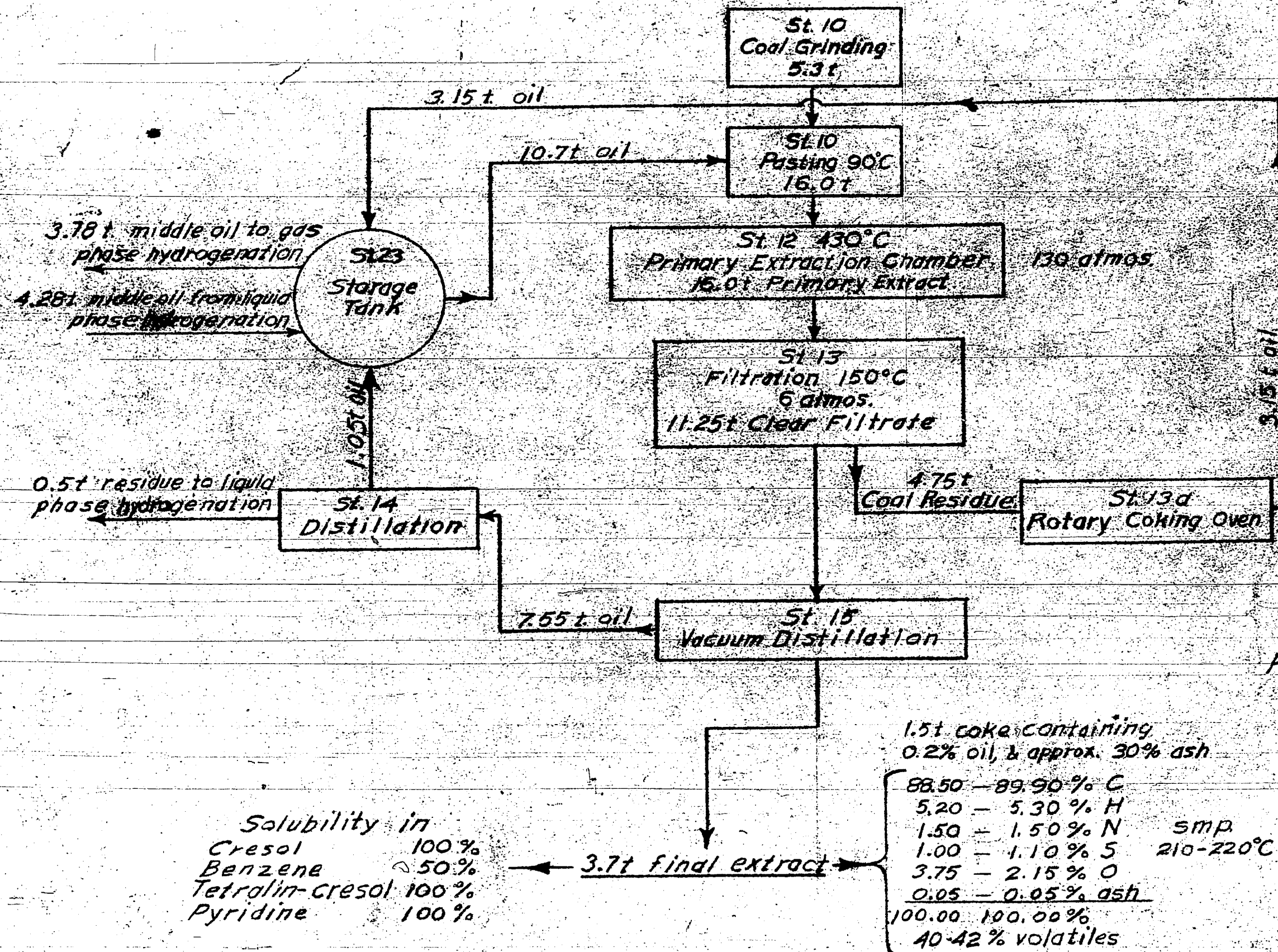
In St-15 the solvent was removed from the ash- and solid-free extract (filtrate) in a two-step vacuum distillation. The residue remaining after vacuum distillation was drawn off in liquid state, chilled with water, and carried on conveyor belts to the shipping room. The product had a melting point of about 230°C., ash content below

0.05 percent, and water content below 1 percent. For separating the heavy oils boiling over 320°C. the total oil was redistilled in St-14. Part of the middle oil resulting from this distillation was returned to the extraction process and the remainder to vapor-phase hydrogenation. The small amount of residual heavy oil, boiling over 320°C., was charged to sump-phase hydrogenation.

The gases obtained when the crude extract leaving the reaction chamber was released from the high reaction pressure were sent to the waste gases from the high-pressure hydrogenation plant for recovery of the hydrocarbon products.

Translated by W. Oppenheimer
January 1947

Research and Development Division
Office of Synthetic Liquid Fuels
Fuels and Explosives Division
U.S. Department of the Interior
Bureau of Mines
Central Experiment Station
Pittsburgh, Pennsylvania
2/10/47
igf



Initial coal had 5-10% water and 5-7% ash. Composition on m.o.f. basis:

- 86.7% C
- 5.1% H
- 1.2% S
- 1.6% N
- about 5.4% by difference
- 100.0%
- 27-28% volatile matter
- The dried coal had 0.5% H₂O.
- Screen analysis:
- 65% < 10,000 mesh/cm²
- 95% < 4,000 mesh/cm²

Figures are tons per hr; 7200 hours per year

BUREAU OF MINES, PITTSBURGH, PA.
SYNTHETIC FUELS R & D DIVISION

DATE: 2-12-47 Figure 1-
 Flow sheet for Pitt-Broche extraction plant having an annual output of 26,000 tons.

DRAWN BY: SN APPROVED: _____
 CHECKED BY: _____

SK-120-A

Solubility in

- Cresol 100%
- Benzene 50%
- Tetralin-cresol 100%
- Pyridine 100%

1.5t coke containing
 0.2% oil, & approx. 30% ash

- 88.50 - 89.90% C
- 5.20 - 5.30% H
- 1.50 - 1.50% N
- 1.00 - 1.10% S
- 3.75 - 2.15% O
- 0.05 - 0.05% ash
- 100.00 100.00%
- 40-42% volatiles

High Pressure Hydrogenation Gases

The gases formed as a by-product during the high pressure hydrogenation are chiefly the saturated hydrocarbons CH_4 , C_2H_6 , C_3H_8 and normal and iso C_4H_{10} . Besides, depending from the raw material, varying amounts of H_2S , NH_3 , CO_2 and CO are formed.

The composition of the gaseous hydrocarbons, i. e. the percentage of CH_4 , C_2H_6 , C_3H_8 , n and i - C_4H_{10} depends chiefly on the reaction temperature and the catalyst. As a general rule the content of higher hydrocarbons, as butane and specially isobutane increases with decreasing reaction temperature and approximately in the following sequence of practically used catalyst groups: oxides and oxide and carbon supported catalysts, sulphides, catalysts on active silicate supports.

During the operation of commercial hydrogenation (and DHD) plants in Germany the following (see Table 1) average and approximate hydrocarbon gas compositions were found:

TABLE 1

a. Liquid phase.

Raw Material	a. Liquid phase.		
	Ruhr	Bituminous Coal Upper Silesia	Lignite Tar
% (wt) CH_4	26	26	28
C_2H_6	24	24	23
C_3H_8	32	32	31
C_4H_{10}	18	18	78
% i- C_4 on total butane	25	(13?)	22

b. Vapour phase.

Catalyst	Carbon support	Silicate support	Sulphide support	Silicate support	DHD oxide support
Temperature	~ 500°	~ 500°	~ 400°	~ 400°	~ 510°
% wt CH ₄	19	22	74	1	21
C ₂ H ₆	23	18	11	1	26
C ₃ H ₈	37	29	31	18	27
C ₄ H ₁₀	21	37	44	80	26
% i C ₄ /total C ₄	18	30	50	75	33

The gases formed during the hydrogenation as well as the inert gases (H₂, CO, CH₄) introduced with the make up hydrogen into the hydrogenation gas circuit must be removed from it as far as it is necessary to maintain the desired hydrogen partial pressure. A certain amount of these inert gases is dissolved in the hydrogenated product. The removal of inerts in this way is often, e.g. in most gasphase operations, sufficient. If this is not the case, the most economical way is an additional scrubbing of the recirculation gas with oil under operating pressure. For the calculation of the final hydrogen partial pressure and the amount of scrubbing oil the solubility coefficients (Henry's law) of H₂ and the inert gases must be known. They were determined in experiments with pure gases or derived from pressure gas analysis and gas quantity in operating hydrogenation units. In the following tables 2 and 3, solubility coefficients from these two sources are listed. It may be remarked that they normally decrease with increasing pressure and that the presence of highly compressed hydrogen reduces the solubilities of other gases. The use of different solvents has shown that the solubility in oils with lower specific gravity is higher.

Table 2
Solubilities of Pure Gases

	1)	2)			
	(Volume Gas per Volume Oil per Atm)				
	<u>a. Hydrogen</u>				
Oil	Heavy Naphtha (0.823)	Gasoil (0.840)	Gasoil (0.840)	1000	Heavy Oil (0.916)
Pressure atm	200	50	200	1000	200
Temp. °C					
20	0.058	0.06	0.055	0.048	0.046
100	0.08	0.08	0.073	0.066	0.058
200	0.126	0.12	0.122	0.11	0.09
(300)		(0.16)		(0.15)	(0.14)
	<u>b. Nitrogen</u>				
20	0.10				0.06
100	0.12				0.08
200	0.16				0.11
	<u>c. Methane</u>				
20	(0.4)		0.34		0.28
100	(0.37)		0.29		0.26
200	(0.34)		0.25		0.24

1. Gas Volume at 15° C and 735 n/per Hg.

2. Technical atm = 735 n/per Hg.

TABLE 3a

Approximate gas solubilities in liquid phase bituminous coal hydrogenation.
(liters (1) gas per kg oil and atm. (2)).

Pressure atm.(2)	Cold catch-pot product Sp. gr.=1		Hot catch- pot oil Sp. gr.=1.2		Scrubbing Oil Sp. gr.=0.85	
	700	300	700	300	700	300
		Pressure release 700 → 25 300 → 20			Pressure release 700 → 25 300 → 20	
H ₂	0.08	0.08	0.1	0.11	0.1	0.1
CO ₂	(1.5)	1.5	2.5	0.3	1.5	(4)
CO	0.08	0.1	0.15	0.1	0.13	(0.2)
N ₂	0.07	0.08	0.15	0.1	0.13	(0.2)
CH ₄	0.2	0.25	0.4	0.2	0.5	0.6 (0.6)
C ₂ H ₆	0.6	0.7	2	0.5	2	3 (3)
C ₃ H ₈	1.0	2.1	5	(0.4)	3.5	11 (12)
C ₄ H ₁₀	3	3.8	20	(0.4)	6	40 (50)
C ₅ H ₁₂	(10)	(10)	(50)	--	--	(80)
H ₂ S	1.9	--	--	--	2.4	(5) --

(1) At 15°C and 735 mm Hg. (Mol. Vol. 24.4)

(2) at 735 mm Hg.

TABLE 3b

Approximate gas solubilities in vapour phase hydrogenation.
(libers(1) gas per kg oil and atm(2)).

Pressure atm(2)	Hydrogenated Product	
	Sp. gr. ~ 0.8	Sp. gr. ~ 0.83
	300	700
		Pressure release 300 → 20
H ₂	0.12	(0.8) 0.11
CO ₂	1.5	-- (5)
CO	(0.2)	(0.8) (0.15)
H ₂	(0.2)	(0.3) (0.15)
CH ₄	0.6	0.8 (0.5)
C ₂ H ₆	1.5	4 (2)
C ₃ H ₈	2.5	15 (5)
C ₄ H ₁₀	10.0	(60) (11)
C ₅ H ₁₂	15.0	(100) --
H ₂ S	(3)	--

(1) At 15° and 735 mm Hg. (Mol. Vol. 24.4)

(2) at 735 mm Hg.

For the calculation of the hydrogen partial pressure in the recycle gas besides the solubility coefficients from tables 3a and 3b the following data must be known: gas formation and composition with regard to the quantity of hydrogenated product, the specific weight thereof, the hydrogen consumption and hydrogen analysis. Then the calculation is made according to Henry's law. If it shows that the hydrogen partial pressure without scrubbing is too low, different quantities of scrubbing oil are assumed until the right hydrogen partial pressure can be intrapolated. If the solubility coefficient of the scrubbing oil differs from those of the hydrogenated product, the gas composition is obtained by trial and error. An easier way for the calculation is then to assume that scrubbing oil and hydrogenated product have the same solubility coefficients. After termination of the calculation the scrubbing oil quantity must naturally be corrected according to the actual solubility coefficient.

The hydrogenated product as well as the scrubbing oil are released from working pressure usually in two stages. In the first stage (release to 20-50 atm) lean gases are obtained, the bulk of propane, butane and light gasoline remaining dissolved in the liquid product. These gases escape partly in the second release stage at about atmospheric pressure respectively in the stabilization plant. The scrubbing oil is normally, after release to atmospheric pressure, in addition evacuated to about 0.1 atm to avoid an undue concentration of light ends in the recirculation gas.

The calculation of the release gas quantities and compositions is made either according to Henry's or Raoult's law. For the calculation according to Henry's law the solubility coefficients obtained during pressure release must be used. The results of both computation methods are in good agreement; the calculation according to Henry's law is somewhat simpler.

The following formulas were used for the calculation:

a. Henry's Law.

$$p = \frac{v}{\lambda \cdot V}; \quad P = \sum \frac{v}{\lambda \cdot V}$$

whereby is:

P = release pressure

p = partial pressure of a constituent in the released gas.

v = volume of constituent in cbm (normal conditions = 15°C, mm H_g) dissolved in 1 cbm of hydrogenated product before pressure release.

λ = solubility coefficient

V = gas quantity set free from 1 cbm of oil. It has to be assumed.

$p \cdot \lambda$ = quantity of a constituent which remains in the product

p · V = quantity of a constituent which is released.

b. Raoult's law.

$$\sum z = 1 = \sum \frac{a f}{\pi g} + P ; \sum x = 1 = \sum z \frac{P}{\pi}$$

whereby is:

z = Mol-fraction of a component in the gas.

x = " " " " " " liquid.

a = " " " " " " original product before release

f = " " " of the condensate.

g = " " " released gas.

π = vapour pressure of a component

P = total pressure.

Beginning of condensation: $f = 0, z = a$

$$P = \frac{1}{\sum \frac{a}{\pi}} = \frac{1}{\frac{a_1}{\pi_1} + \frac{a_2}{\pi_2} + \dots + \frac{a_n}{\pi_n}}$$

Termination of condensation: $g = 0, x = a$

$$P = \sum a \cdot \pi = a_1 \pi_1 + a_2 \pi_2 + \dots + a_n \pi_n$$

Washington, D. C., 10 Feb 1947

E. E. Donath