IG-Norm 10-24. Corrosion-and Acid-Proof Steels.

Covers designation, composition, mechanical properties and recommended use of austenitic CrNi-steels with additions of Mo, Si, or Cu, particularly Krupp V4A, V6A, V8A and V16A.

IG-Norm 10-30. Scale-and Heat-Resistant Steels.

Covers designation, composition, mechanical properties and recommended use of martensitic and ferritic CrSi-Al,-or Ni-steels, with addition of Ti, Mo, W or V.

IG-Norm 10-31. Scale-and Heat-Resistant Steels.

Covers designation, composition, mechanical properties and recommended use of austenitic CrMn-Si-Ni-steels with additions of Ti or N_2.

IG-Norm 10-32. Scale-and Heat-Resistant Steels.

Covers designation, composition, mechanical properties and recommended use of austenitic CrNi-steels with additions of Si or Mo.

U. S. BUREAU OF MINES T-180
HYDRO. DEMON. PLANT DIV.

CATALYSTS IN THE PRODUCTION OF SYNTHETIC FUELS FROM COAL

by S.B. Tatarskii, K.K. Papok and E.G. Semenido.

Neftanoie Khozyaistvo, vol. 24, #2, 1946 pp. 52-55

(Second article. Results of study of materials of a Russian Commission for the study of synthetic fuels in Germany, July, 1945).

The importance of the catalyst is exceptionally great in the production of synthetic fuels and oils.

A knowledge of catalystsand of the conditions for their use is like having a key to unlock production secrets of the synthetic fuel manufacture, which has been widely used in Germany.

It is difficult to hide from an observer's eye the 18 m converters, sizes of furnaces or the different equipment, which are integral parts of the synethtic plants, while when telling about catalysts secrets are easily kept, which makes it not impossible, that the information given us by the German specialists will contain some inaccuracies and omissions.

CATALYST FOR THE HYDROGENATION OF COALS AND OF THE PRODUCTS OF THEIR THERMAL TREATMENT.

The preparation of catalysts resistant to poisoning with sulfur, to be used in the hydrogenation of coal and of the products of their thermal decomposition, was the turning point in the development of synthetic fuel manufacture after which the development of industrial hydrogenation was quickly brought to conclusion. It has, however, been found necessary to forego the hydrogenation in one single step, because of the necessity of working with very low partial pressures of the material (and therefore also with small yields of the finished product) in order to avoid the poisoning of the catalyst with asphaltic products. This has caused the breaking up of the process into two steps, the liquid phase and vapor phase hydrogenation.

Heavy oil (init. b.p. 320 - 360°C) was hydrogenated in the liquid phase in the presence of powdered iron catalyst at 450° C and at pressures of 275 - 700 atm. Coal, in a paste form, was hydrogenated under similar conditions. The used-up iron catalyst was continuously removed from the cycle and replaced with fresh catalyst. The catalyst was not regenerated.

Middle oil, b.p. 200 - 350°C was hydrogenated in the vapor phase. The hydrogenation temperature was 420 - 450°C, with 300 atm. pressure and a fixed bed catalyst (tungsten sulfide).

Catalysts used in the hydrogenation were principally prepared in two main factories, which belonged to the I.G. Farbenindustrie A.G. One of these was located in Ludwigshafen, the other one in the town of Leuna near Merseburg (Leipsic).

These factories made new, and regenatated old catalysts returned by the hydrogenation plants in exchange for new. In addition to these two catalyst factories there were two others located near the plants in Pölitz and Schwarzheide. These latter two factories furnished catalysts only for their own plants.

Detailed study of the work in the factories at Leuna and in Pölitz was made difficult by the absence of the technical personnel and the accounting office.

A. Liquid Phase Catalysts.

"Catalyst I". Bog iron ore, or other material containing dispersed iron oxide, such as the lauta mass (a by-product of the Bayer's method of manufacture of alumina, containing about 35% iron oxide), the ash from Winkler gas producers working on powdered fuel, etc., were used as catalysts in the liquid phase hydrogenation. This was designated as Kontakt I and 9% of it by weight of coal used was added.

"Catalyst #10927, or "Kontakt II". When tar was hydrogenated, a carrier consisting of iron oxide saturated with hydrated ferric oxide was used as catalyst. Carriers were substances used as "Kontakt I". Saturation was done by wetting with a solution of ferrous sulfate and sodium hydroxide, taken in equivalent amounts, in a way to produce 5% precipitated hydrated oxide of iron (as metallic iron). Such a catalyst was listed as #10927, also known as "Knotakt II".

The fresh catalyst was introduced as a paste, in an amount of 0.2 - 0.5% of the weight of the tar. The total proportion of the catalyst paste and tar, used during hydrogenation, was considerably higher: 3 - 4 m^3 of paste was used for 20 - 25 m^3/hour of tar, the paste containing 30% of the dry catalyst powder.

Catalyst "Kontakt III". We have found indications in many plants that when low sulfur raw material was hydrogenated, "Kontakt III" was added, which contained sulfur either as sodium sulfide, or as elementary sulfur (about 0.1 - 0.3% of the raw material). An insufficient sulfur content in the raw material would cause a lowering of sulfur in the prehydrogenation catalyst, which would reduce its activity.

Catalyst 11002. Before the use of catalysts I and II (prior to the outbreak of the war) a few of the plants hydrogenating tar used a powdered molybdenum catalyst, listed as 11002. We have not succeeded in collecting information on its preparation, and we only know that its molybdenum content was low, 2 - 3%. Change from the molybdenum to the iron catalyst was caused by the difficulties of obtaining molybdenum during the war.

B. Catalysts for the Vapor Phase Hydrogenation.

The pre-hydrogenation catalyst #5058 was pure tungsten sulfide (WS_2). It replaced molybdenum sulfide because of its 4 times greater activity. The amount consumed was 0.09% of the hydrogenated middle oil.

One converter charge, weighing 19 - 20 te was sufficient for the production of 60,000 te of products. The life of the catalyst was 200 - 400 days. The cost of the catalyst was RM 33,890 per te.

Preparation of the catalyst. A mother liquor of ammonium sulfide was prepared (from 14% solution of hydrogen sulfide and 12 - 13% ammonia water) for the solution of tungstic acid (called the yellow earth in the preparation directions). 350 - 400 kg "yellow earth" is used for 1100 li. ammonium sulfide solution. The mixture was stirrred while heating to 70°C, and then settled for two hours. The solution was filtered, sent to the saturator and heated to 50°C. Hydrogen sulfide was next bubbled through. The yellow salt (ammonium sulfo-tungstate) began then to precipitate and the temperature was raised to 70° during one half hour. The saturator was next slowly cooled (4° per hour), while passing hydrogen sulfide continuously, the pressure of the hydrogen sulfide being kept 380 - 300 mm Hg. The yellow salt kept coming down continuously. The saturated solution was cooled to 15 - 20°C.

Should the solution leaving the saturator contain an insufficient amount of ammonia, more ammonia was added to the saturator, while cooling it with cold water to avoid overheating.

The solution must at all times contain 14% hydrogen sulfide and 12% ammonia. 400 kg "yellow earth" produces 500 kg yellow salt. The saturator was opened after the salt had crystallized and the solution with the precipitate was suction filtered. The salt remains on the filter cloth, the soltuion was collected. The salt was transferred from the filter cloth to a drier with a stirrer and dried for three hours at 130°C. The drier was heated with a steam jacket. The escaping gases (hydrogen sulfide, ammonia) were absorbed in recirculating water.

After drying the salt was dried to 20° (by water circulating through a cooling coil) and the drier emptied into a worm-driven furnace. It took the salt two hours to pass the furnace. Water gas (5 - 6 m^3) was passed through the furnace. The worm was operated at the same speed as with other catalysts: three 180 kg. drums in eight hours. The salt which left the furnace was yellowish black. As soon as the drum was filled with the salt, it was covered to prevent oxidation of the salt. When the powder was cold, it was sifted through a 1/2 mm screen and ground in an atmosphere of nitrogen. The ground powder was compressed into tablets and the catalyst was ready for use.

The preparation of the catalyst 8376 was begun during the war, because of the shortage of tungsten. Its composition was: 18% tungsten, 2% nickel, 80% alumina (carrier). Its consumption amounted to 0.03 kg/te hydrogenated middle oil. The catalyst charge in the converter is 6 - 7 te. The catalyst can hydrogenate up to 60,000 te middle oil. The cost of the catalyst was RM 17,432/te.

Preparation of the catalyst. 200 liters water was poured into a cooled container and 1500 kg aluminum sulfate added. The salt was stirred and heated to 60 - 70°C with live steam. After settling for two hours the solution was pumped over into an other vat and from there into a mixer where ammonia was added while heating to 90°C. The hydrated alumina was filter-pressed, washed for 8 - 10 hours and transferred to driers where it was heated for 8 - 10 hours with high pressure steam. When dry, the product was ground and sifted through 6 mm screens. The sifted product was tabletted to a pressure resistance of 20 - 25 atm.

The tablets were ignited in a vertical electric furnace at 890 - 902°. They were next saturated with a solution of tungsten and nickel and dried at 80 - 90°. The saturation was doen three times. The saturated tablets were reground and sifted through 3 mm screens. The powder then entered a worm driven furnace with three compartments. Two of them were heated from the outside, the third one was the cold zone of the furnace. The powder was kept in the furnace for 1 1/2 - 2 hours. Hydrogen sulfide and pure water gas were then introduced while the worms rotated uniformly and moved the powder downwards. The gases were scrubbed with sodium hydroxide to absorb the hydrogen sulfide. The waste liquor contained 6 - 8% hydrogen sulfide and up to 6% ammonia. About 5 m^3 hydrogen sulfide was run through in one hour, and somewhat less water gas (3.5 - 4 m^3).

The powder must be pure black when finished, and was then transferred from the furnace to the tablet press. The tabletted catalyst was once more ignited in an electrical vertical furnace at 920° C in a stream of hydrogen sulfide. The tablet machine operated under a pressure of 50 - 60 atm. Three drums of 180 kg each of the 8376 catalyst were made in 8 hours.

Hydrogen sulfide was produced in a special generator from sodium hydrosulfide and 75% sulfuric acid.

Benzination catalyst 6434. Its composition was 20% tungsten and 80% carrier (Bavarian activated earth, called "Terrana"). The catalyst may be used for up to 3.5 months. The amount consumed was 0.07 kg/te gasoline.

Method of preparation. 250 kg bleaching earth "Terrana" was added to a mixer, then 300 liters diluted hydrofluoric acid (160 kg acid to 1000 li. water). The mixture was mixed for 30 minutes and 600 liters of the mother liquor of ammonium sulfotungstate was added, while running the mixer and heating to 80 - 90°. The product was dried after 8 - 9 hours of such treatment, and then cooled to 20°. The product was next transferred to a mill, ground, and sifted through a 6 mm screen. It was next sent to a worm-driven furnace where it was heated in an atmosphere of hydrogen sulfide (6 m^3) and water gas (5 m^3) to a temperature of 920°C. The thermal treatment lasted for 2 hours. The product was groundupon leaving the furnace, mixed with a small amount of water and tabletted. The tablets were sifted, dried in a furnace for preliminary treatment (at 320 - 400°) for about 2 hours. They were then reheated in a vertical furnace to 1040 - 1080°C in an atmosphere of hydrogen sulfide (6 m^3) and water gas (5 m^3). This heat treatment also lasted two hours.

Catalysts for Hydrogenation Products.

The insufficiently high octane number of the hydrogenation gasoline, (70 - 72), which was the principal source of German aviation gasoline, has caused the German motor fuel industry to find means of raising that number. This was done in two ways: by means of catalytic aromatization(dehydrogenation) of the hydrogenation gasoline (the so-called DHD installations) and through the production of isobutane (polymerization of isobutylene and the alkylation of isobutane with butylene).

The principal features of both these methods were solved by the use of catalysts.

Catalyst 5633 was used for the catalytic aromatization of gasoline to raise the octane number of the hydrogenation gasoline. The catalyst was composed of 5% molybdenum oxide and 95% alumina (according to data obtained in Leuna, according to information from the town of Most, molybdenum oxide formed 9% of the catalyst.

Method of Manufacture. The technical grade of aluminum oxide was plasticized with water and nitric acid in a kneading machine, and shaped into cubes on a roller press. The cubes were dried and ignited at 450° C. The cubes were saturated with a solution of ammonium molybdate in such a way as to leave 5% molybdenum oxide in the finished product.

Catalyst 6448 was used for the dehydrogenation of butane into butylene. It was composed of 90% alumina, 2% potassium oxide and 8% chromium oxide.

Method of manufacture: 22.5 kg activated alumina (list number 5780) 2 kg of an other activated alumina (list number 5780-100), a calculated amount of potassium hydroxide, chromic anhydride, as well as 2 1/2 liters of 62% nitric acid and 7 - 9 liters of water were mixed for 40 minutes in a mixer, formed into balls, dried for 16 hours at 150° and ignited for 4 hours at 450° (to destroy the nitrates).

The polymerization of isobutylene into isooctylene was made with the help of catalyst 2730, consisting of activated carbon saturated with phosphoric acid, and consisting of 35% phosphoric acid, 60% carbon and 5% water.

Method of Preparation: 8 kg of activated carbon were mixed with 5.12 kg phosphoric acid and 4 liters of water. The mixture was permitted to stand until the carbon was soaked through, and dried at 80 - 100°.

Catalyst 4821 was used for the polymerization of isobutylene. The catalysts consisted of asbestos saturated with pyro-phosphoric acid, (25% asbestos, 75% pyrophosphoric acid). Orthophosphoric acid was concentrated at 260° for the conversion into pyrophosphoric acid; 16 liters of the pyrophosphoric acid were mixed with 8 kg. asbestos, the mixture shaped and dried for 60 hours at 150°.

Catalyst 3076 was used for the hydrogenation of isooctylene and isooctane. It was composed of 1 molecule of nickel sulfide and 1 molecule of tungsten sulfide.

Method of Preparation: 50 kg nickel were dissolved in 60% nitric acid and precipitated with soda (90 kg). The carbonate was filtered, washed, dried, ground and sifted.

50 kg tungstic acid (H_2WO_4) was added to 25 kg nickel carbonate and 25 kg of water. The mixture was stirred and evaporated to a thick paste, dried counter currently for 12 hours and ignited at 400°. The mixture was next ground, after having about 1% graphite added to it, compressed, reground and compressed into 10 mm tablets.

CATALYST FOR THE FISCHER TROPSCH GASOLINE PROCESS

The calculated composition of the catalyst: for every 100 g. metallic cobalt there was
5 g thorium dioxide
10 - 11 g. magnesium oxide
200 g Kieselguhr

The raw materials were used in the form of nitrates. The solutions were kept in separate containers. A mixture of the three nitrates was prepared of the following composition:

$Co(NO_3)_2$	40 g Co/li
$Th(NO_3)_4$	2.4 g ThO_2/li
$Mg(NO_3)_2$	4.4 g MgO/li

The mixture of the nitrates was mixed to 100° and poured rapidly into a solution of soda (104 g/li), also heated to 100°. The volumes mixed were 1.3-1.4 m³. The mixture was then vigorously stirred for 3-4 minutes. Kieselguhr was added next, and the mixture re-mixed. It was next filter-pressed, washed with distilled water until 100 ml wash water were neutralized with 4 mls(sic) 0.1 N sulfuric acid.

The filtered sludge was mixed with the dust residue of the catalyst obtained previously and pressed in a Wolf rotating press.

The pressed mass was dried in a drier (at 96 - 104°) to a water content of 4 - 5%, crushed and sifted into lumps 1 - 3 mm in size. The catalyst was next reduced at 400° for 50 minutes in a rapid stream of hydrogen.

W.M. Sternberg
12/11/46

DR. WINKLER'S REPORT ON AROMATIZATION AT 700 ATM.

Ruhröl G.m.b.H., Welheim in Leuna
January 4, 1941

Dr. Winkler has presented a report on the 700 atm. aromatization. He operated at 630 atm. total pressure, corresponding to 450 atm. hydrogen pressure with a production of 0.4 kg. gasoline per liter of catalyst per hour. An increased capacity appears possible in pilot plant operations, but does not seem probable on a large scale even with the introduction of blends. The concentration of aromatics in the 165° final b.p. fraction from tar middle oil (including 8% of liquid phase gasoline) was 55- 58 percent by weight (or 50-53% by volume). However, recently Dr. Winkler has used catalysts which produced in the pilot plant unit (5 li converter) gasoline from tar middle oil with up to 70% aromatics. The production was 0.4 kg. No information was given on the gasification.

Dr. Winkler gave the following data on the yield:

The losses of the middle oil used were 12.2 - 12.4%. Added to this is the stabilization in Scholven with a gas loss of 3.5 - 5%. The gasoline must in addition be refined with sulfuric acid and redistilled. For these operations Dr. Winkler gives but a small additional loss of about 1/2%. These figures lead a total C gasification of about 17.6 - 19%, calculated to gasoline + gasification*. These figures are in agreement with those obtained in Ludwigshafen in a 1-liter converter.

Dr. W. gives an additional information on the yield, by stating that 100 parts m.o. give about 87 parts high compression gasoline, and out of this 82 parts**) refined stabilized gasoline, which leads to a production factor of 1.22.

* The C gasification figures as follows:

100 parts m.o.	with 89.7% C	=	89.7 parts	C
87.7 " gasol.	" 87.5% C	=	76.7 "	C
C loss		=	13 "	C

Added to this are 3.5 - 5 parts of stabilization loss with 80% C = 2.8 to 4 parts C. This figures to a gasification of 17.6 - 19% referred to the 89.7 parts of C taken.

I was unanimously agreed, that a substitution of coal liquefaction products for the tar middle oil will reduce the yield by about 3% because of the lower C content of the middle oil. With coal liquefaction middle oil the yield would be further reduced because a higher gasification of the coal liquefaction middle oil must be taken into consideration if the same percent aromatics is desired from coal as from tar middle oil. Dr. W. stated that with the same operating conditions the gasoline from the liquefaction middle oil would have an octane number lower by 2 - 3 units, than from tar middle oil.

Dr. W. has as yet not investigated the problem of liquid phase gasoline with the coal liquefaction, because only a small amount of high boiling gasoline is obtained in the tar liquid phase. This question is, however, very important when operating with coal liquefaction middle oil, especially if operations in Upper Silesia are to be designed for the production of fuel oil, where about 35% liquid phase gasoline referred to gasoline + m. o. is formed in the liquid phase.

Some other points were discussed, which must be born in mind in the production of aromatic gasoline.

The proportion of isobutane must be mentioned first of all, because in aromatization only a fraction of the amount is formed of that produced in the normal benzination to aviation gasoline, or in the benzination + DHD. Even should the 700 atm. aromatization be performed at lower temperatures, to produce a gasoline suitable for DHD but with lower gasification, less isobutane will be produced, because the temperatures must be way higher than with the present two-step benzination.

Dr. W. corrected also some information from a report to the office namely that the hydrogen consumption per te of gasoline with

** Contrasted with this, the yield in benzination + DHD of 5058/6434 gasoline is 86 parts, of which only 73 parts DHD gasoline can be obtained. We replied, that when liquefaction middle oil is used as the raw material, the yield at 700 atm. aromatization is only 78%, instead of 82. Moreover, with a 300 atm. benzination, the yield set at 86 parts was much too low. We figured at that time that our best DHD catalyst gave a yield of 78 parts, or as much as in the 700 atm. aromatization, and set for the industrial operation a yield of 75 parts.

It must in addition be noted, that the quality of the DHD gasoline from coal liquefaction middle oil is equal to the aromatization gasoline from the tar middle oil, and it has therefore a somewhat better overload production than the aromatic gasoline from the liquefaction products.

165^o end point was 700 m^3, and not 900 m^3 as there give.

Dr. V. will further clarify the problem by obtaining one tank car each of middle oil from Scholven and from Gelsenberg, and will pass through the Ludwigshafen high pressure installation 2 te from each of these tank cars as well as 2 te of his tar middle oil, using 30 li of his catalyst in 10 mm pills. In this way, starting with similar raw materials and using the same catalyst, the yield and the hydrogen consumption during the 700 atm. aromatization will be established. Dr. V. will conduct his tests with the circulation gas, while the tests in Ludwigshafen were conducted with new gas under a different pressure, and with the addition 0.1 -- 0.15% H_2S. Tests with coal liquefaction middle oil were to be run for the production of a gasoline with 50% aromatics. The gasolines were to be refined with 96% sulfuric acid, and redistilled to an endpoint of 165^o and stabilized to a vapor pressure of 0.4 atm.

Dr. V. will in addition send to the high pressure laboratory at Ludwigshafen estimates of the costs of 700 atm. aromatization for the production of 235,000 te gasoline and 120,000 te gasoline.

The average C of the gasification is 2.5; there is a total of 30 - 36% isobutane in the total butane. In a stall with 10.5 m^3 of catalyst there are formed 280 m^3 of hydrocarbons, which are distrmbuted as follows:

(The figures refer to "high pressure gasification"; the stabilization results are therefore not included here)

C_1	55.3 m^3	recalculated:	20.6% by vol.,	8.8% by weight
C_2	81.8 "		30.3 "	24.4 "
C_3	68.7		25.4 "	30.0 "
C_4	64.0 "		23.7 "	36.8 "
C_5	10.6 "			

The middle oil used had 89.7% C, 9.4% H and 4% phenols.

The stall has 10.5 m^3 of catalyst and is operated on the first day at 24 mv with about 3000 li. m.o. injected with the return, the second day with 6000 li, on the third day with 9000 li. The temperature will be regulated to keep the concentration 50 - 55%, which corresponds to a specific gravity of the catchpot product of 0.830 - 0.840. This will in most cases be obtained with an inlet temperature of 24.8 mv and a maximum temperaturse of 26.2 mv (40^o cold junction). The five li converters are operated at 25.5 mv, as are the large units. The b-middle oil (A.P. -25^o) produces more and better gasoline with higher aromatics, than does the middle oil (A.P. of the gasoline -4 to -5^o), and with the new catalyst the concentration of aromatics is at first somewhat higher than later. It is artificially neutralized right from the start. The new catalyst can also be used at 300 atm, but if the feed is not de-phenolated the efficiency of the catalyst becomes lower.

The cost of the catalyst is RM 1200 - 1500 per m^3. Recovery of the catalyst would not pay, its life being six months to one year.

Dr. W. added that the liquid phase production is greater at lower, than at higher pressures. He attributes it to the difference in the H_2S content of the circulation gas, and gives the following data:

90% H_2 corresponds to 0.05% H_2S

71 - 75% H_2 " 0.1 - 0.15% H_2S (450-470 atm of H_2)

W. M. Sternberg.

D

TOM Reel 130
Pgs. 508-558

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-182

KCBraun
11/29/46

Abstract of Bid on Plant Producing 180000 t/ann. Aviation Gasoline & 30000 t/ann Liquid Gases from Brown Coal by Catalytic Pressure Hydrogenation, for Russia

I. G. - Ludwigshafen, Dec. 1939

Index

I. Basis of Bid.

This bid covers the furnishing of all equipment. The use of our process experience and patents is the subject of a separate agreement.

The bid is based on using brown coal poor in bitumen of about the following composition:

3% water when dry,
13% Ash in the dry coal,
68.5% C in the pure coal,
54% Volatiles in pure coal,
10% crude tar in pure coal.

It was assumed that the coal would be delivered free of sand and gang. Inasmuch as the coal will probably contain 30-40% water as delivered and a dry coal containing 3% water is required for gasoline production and one containing 8% water for gas production, a coal drying plant is included in the bid. It was also assumed that this plant would be a complete and independent unit, including power plant, water works, work shops, laboratories, etc.

In order to avoid spare equipment, the individual departments of the plant are so layed out that the required annual production can be produced in 330 operating days, which will provide 35 days for shut-down and repairs.

The bid covers the delivery of all equipment for the complete plant, f.o.b. a Baltic port. Costs of buildings and equipment installations are based on present costs in Germany. The cost of possible German construction supervisors is not included.

When using the brown coal above specified, the completed plant will produce aviation gasoline of these characteristics: -

Spec. gravity @ 15° C		0.728
Aniline point		48°C
Boiling curve:	Begin boil	46°C
	@ 70° C	17%
	@ 100° C	58%
	End boil	149°C
Vapor press. according to Reid @ 38°C		0.5
Octane number CFR motor method		72
CFR motor method, 0.09 Vol. % Pb		88

II. Gasoline Plant

The coal is processed in 2 stages:

1. Liquid phase,

2. Vapor phase.

In the liquid phase, the coal which is made into a paste and mixed with finely distributed catalyst, is processed to middle oil. In the vapor phase, the middle oil in vapor form is passed over the catalyst in a fixed position, during which process most of it is transformed into gasoline. The untransformed middle oil is returned to the vapor phase with the fresh feed.

The coal is first crushed and dried. Then it is made into a paste with pasting oil and then ground. The catalyst is added here. The coal paste contains about 50% solids, of which a maximum of 1% will be retained on a 400 mesh screen, and can be readily pumped when heated to about 100° C. The coal paste is compressed in paste presses to 700 atm and injected, together with compressed H_2, into the converters built into stalls. The heating is done partly in heat exchangers, partly in gas fired preheaters. In the first stage, about 99% of the coal is reduced to middle oil, gasoline and vaporous carbo-hydrates.

From the converters, the products of reaction are separated in a catchpot, from which the heavy liquid oils, together with small residual coal and ash, is drawn off at the bottom. The lower boiling oils, together with the reaction gas, are taken off at the top, from where they pass thru the heat exchanger, giving up their sensible heat to the converter feed. The cooled vapors then pass thru a cold catchpot, where the reaction gases are separated from the liquid products. The reaction gas then passes thru an oil wash for the removal of included vaporous carbo-hydrates and is returned mixed with fresh H_2 in the circulating lines to the heat exchangers. The wash oil is decompressed in stages in order to separate the H_2--rich from the H_2-poor gases.

The liquid products from the cold catchpots are decompressed in stages for the same reason, separated from the water and decomposed by distillation. Two fractions are produced: gasoline and middle oil, boiling to about 325° C, and heavy oil, boiling above 325° C. The heavy oil is used as pasting oil for coal. The gasoline and middle oil concentration in the catchpot is about 55% by weight.

The let-down sludge collected in the catchpot is diluted with a part of the distillation heavy oil and centrifuged, in which process most of the oil is separated from the solids. The oil contained in the centrifuge residue is recovered in a revolving kiln (low temperature carbonization) by heating the kiln and adding steam to the residue. The heavy oil produced in centrifuging and low temperature carbonization, together with the residual distillation heavy oil, is used as pasting oil.

The liquid phase gasoline is refined in the vapor phase by passing it, together with the middle oil, over the vapor phase catalyst. No additional reaction space is required for this.

The vapor phase feed is compressed to 300 atm by injection pumps, which force it, together with H_2 thru the heat exchanger and preheater to the converters, where it passes in vapor form over the catalyst. On leaving the converters, the gases and vapors give up their sensible heat in the heat exchangers. After cooling, gasoline and middle oil are condensed in a catchpot, the H_2 is returned to the reaction in the circulating lines, and the liquid products are decompressed in stages and decomposed by distillation into untransformed middle oil and gasoline. In the stagewise decompression H_2-rich gases are first given off, then gasoline-rich gases.

The vapor phase process uses 2 different catalysts. The liquid phase products first pass over a refining catalyst. The gasoline produced here is separated and the refined middle oil is decomposed by the second catalyst. The second, strongly splitting, catalyst decomposes the middle oil up to 50% gasoline in a single pass. The oil not split is returned to the process. A total of 80% by weight, based on liquid-phase product fed, of aviation gasoline is produced in the vapor-phase.

The raw gasoline produced in the vapor phase and separated in the following distillation is first stabilized to free it of its gaseous constituents and standardize the desired vapor pressure of the finished gasoline. The stabilizing column operates at a pressure of 15-20 atm, depending on the temperature of the available cooling water. The vapors leaving the head of the column are condensed to the extent required for return run. The uncondensed portion goes to the debenzination plant.

The stabilized gasoline leaving the lower part of the column is first washed in lye to remove its acid constituents and then in water to remove the lye. The gasoline is separated from the washing liquid in separators and the lye is returned to the washing process. The washed gasoline goes to storage.

The off-gases produced at various points in the liquid and vapor phase go to two separately operating debenzination plants to recover the pentanes and the higher carbo-hydrates. These gases are first desulfured. The desulfured gases are then compressed to 20-25 atm. absolute and piped thru heat exchangers to pressure columns where a part of the condensate enters the top of the column as return run to get the required sharpness of separation; the rest is drawn from the separator and goes to the liquid gas producing plant.

The gasoline produced in debenzination and originating from the vapor phase off-gases goes to the raw gasoline for stabilizing, that originating from the liquid phase off-gases is added to the injection feed of the vapor phase for refining.

The mixture of low carbo-hydrates, hydrogen and inert gas from the debenzination plant is decomposed into liquid gas consisting of butane and propane and into residual gas in a separating apparatus similar to the stabilizing plant. The liquid gas produced is stored in tanks @ 25 atm. The residual gas goes to the splitting unit of the gas producing plant.

The gasoline plant includes the following departments:

1. <u>Coal Preparation Dept:</u>

   a. <u>Drying:</u>

      Various steam dryers for drying raw coal from 30-40% to 8-3% water.

   b. <u>Unloading and Storage:</u>

      Coal and catalyst bunkers, various unloading and distributing devices.

   c. <u>Crushing and catalyst equipment.</u>

      4 groups, each consisting of: crusher, pump, vibrating screen, mixer, weighing feeders, and double roll stands.

2. <u>Paste Press Dept. for 700 atm:</u>

   18 paste presses, various pumps with motors for hydraulic drive of paste presses, surge tanks (Pufferflaschen), various mixers.

3. Gas Circulating Pump Dept. for 700 atm:

5 circulating pumps with electric drive, 1 cooler, 1 crane.

4. Coal stalls for 700 Atm.

3 stalls, each consisting of:

4 H.P. converters, 1000 mm dia. x 18 m lg, 3 heat exchangers, 600 mm dia. x 18 m lg, 1 hot gas separator (hot catchpot), 1000 mm dia. x 9 m lg, 1 product separator (cold catchpot), 1000 mm dia. 1 product cooler, 1 let-down (sludge) cooler, 1 gas preheater, 2 hot gas blowers, etc. 1 special stall crane, 200 t, 22 m span, 25 m lift.

5. Circulating Gas Wash for 700 atm:

3 H.P. washers, 1000 mm dia. x 12 m lg, 3 expansion machines, 4 booster compressors with electric drive, gas cooler, separators, expansion tank, crane, etc.

6. Gas Circulating & Injection Pumps for 325 atm:

4 gas circ. pumps, injection feed pumps, 3 injection water pumps each with electric drive, surge tanks, washer, crane, etc.

7. Gasoline Stalls for 325 atm:

4 stalls with a total of
12 H.P. converters, 1000 mm dia. x 18 m lg,
8 heat exchangers, 1000 mm dia. x 18 m lg,
4 preheaters, 4 catchpots - 1000 mm dia,
4 coolers, etc.

8. Residue Centrifuging:

36 centrifuges with electric drive, steam-pumps, coolers, let-down expansion tanks, etc.

9. Residue Carbonization (Low Temperature):

Mixing tanks, steam pumps, traveling crane, 10 groups each of revolving gas heated kiln, dust separator & cooler.

10. Emergency Expansion (Decompression):

Emerg. exp. tower, pumps with drives, partly electric and partly steam, pipe lines, tanks, etc.

11. Protecting Gas Plant:

1 - 1000 m^3 N_2-tank, 1 - 3000 m^3/h respiration tank, N_2-compressors, CO_2-turbo-blowers each with electric drive, pipe lines, valves & fittings.

12. Distillation:

2 coal catchpot distilleries, each 35/t/h,
3 gasoline catchpot distilleries, each 28/t/h,
tube heaters, fractionating towers, condensers, heat exchangers, separators (catchpots), pumps with motors.

13. Two Stabilizing Units, 2 Gasoline Washing Units, 2 Debenzination Units, 1 Liquid Gas Producing Unit with Storage Tanks.

14. Storage Tanks:

for heavy oil, light oil, intermediate and sales storage, consisting of:
10 tanks each 500 m^3
17 tanks each 1000 m^3
6 tanks each 2000 m^3
2 tanks each 5000 m^3
and filling station for tank cars, fomite fire exting. equipment, etc.

15. Pipe Lines within Buildings.

Measuring Instruments.
Electrical Installations.
Buildings and Contingencies.

16. Connecting Lines Between Buildings.

III. Gas Production.

The gas production plant, consisting of H_2 and fuel gas plants, must produce the H_2 required for gasoline production and the fuel gas for the whole plant.

<u>H_2 Plant:</u>

Of the total of 71000 m^3/h (15°C @ 1 atm) H_2 required, about 36000 m^3/h are recovered from hydrogenation off-gas freed of gasoline constituents by a catalytic splitting process.

The gases produced in liquid and vapor phase gasoline production are first carefully desulfured. The gas if freed of inorganic sulfur by a low pressure washing process, followed by a dry fine cleaning with a Lux mass (by-prod. of alum. mfg.), and the pure sulfur is recovered in an auxiliary plant. The organic sulfur is removed by a special catalytic process. The sulfur-free gas is then split up into CO, CO_2 and H_2 in retorts, the tubes of which are filled with catalyst, with the addition of steam and external heat. The tube retorts are heated by fuel gas and the waste heat is recovered to generate the steam required. A Winkler process H_2 generating plant, in which an N_2-poor gas is produced by continuous gasification of brown coal with the addition of O_2 generates the residual 35000 m^3/h of H_2. The 0-water gas (Nullgas) produced is carefully cleaned of its dust and then desulfured, assuming that the H_2S content of 0-water gas does not exceed 6-7 gr/m^3. The sulfur is recovered in pure form.

The O_2 required for the production of the 0-water gas is produced in a "Linde-Fränkl" air reduction plant. The 0-water gas, consisting largely of CO and H_2, together with the split gas from the tube retorts, goes to a conversion unit, in which the CO is converted to CO_2 and H_2 by the action of the steam added to the catalyst, according to the equation:

$$CO + H_2O = CO_2 + H_2.$$

The heat of reaction in the conversion covers the heat requirements of the process, so that the catalyst retorts need to be heated only at the start of the process. The converted gas contains considerable CO_2, which is removed at 25 atm. absolute in a pressure water washing unit. The 6-stage H.P. compressors force the gas into the washing unit after the third stage. The pressure water required for washing is supplied by H.P. centrifugal pumps to the washing towers. Most of the energy required by the pumps is recovered by expansion in turbines. The gas largely freed of CO_2 is further compressed to 325 atm. by the upper stages of the H.P. compressors.

Before the compressed gas can be used for hydrogenation proper, it must be cleaned of CO in an H.P. gas cleaning unit. This is done by means of copper liquor at a pressure of abt. 300. atm.

This washing liquor is pumped to the washing towers. Most of the energy required for the pumps is likewise recovered in expansion machines (Entspannungsmaschinen). The wash liquor is prepared in an auxiliary apparatus and regenerated after return from the wash circulating system, so that only such losses as occur in the process must be replaced.

About 65% of the total H_2 is required in the liquid phase @ 700 atm. Several booster compressors are provided for raising the raw H_2 pressure from 300 to 700 atm.

Fuel Gas Plant.

To produce the required 53×10^6 Kcal/h of fuel gas, a plant similar to the Winkler process is also provided, in which, however, continuous gasification of the brown coal takes place with the addition of air.

The sensible heat of the Winkler gases is used to produce steam in waste heat boilers just as in the splitting unit. The generator units for producing Winkler 0-water gas and Winkler fuel gas are properly combined in one plant. It is also assumed that a suitable fine coal with grains of 8-10 mm is available for gasification in the Winkler generators.

The Gas Producing Plant includes the following departments:

1. Desulfuring Unit for the off-gases in gasoline production:

   a. Washing Unit:

   2 wash towers, columns, heat exchanger, container, pumps with motors and starters, 1 secondary H_2S burning unit (Nachverbrennungsanlage) with acid-proof stack, 1 sulfur recovery unit with blower house.

   b. Lux mass fine cleaning and catalytic desulfuring unit:

   2 cleaning towers, 1 shut-off tower, 1 cooler, 1 gas heater, 2 blowers with motors, 1 belt conveyor, 6 catalyst containers, 2 cranes.

2. Splitting Unit for the off-gases in Gasoline Production:

   4 retorts or converters each with 66 splitting tubes, 4 heat exchangers, 4 waste heat boilers with pumps, motors and other auxiliaries, 1 crane, 1 stack 90 m high, breeching, 2 flue gas exhaust fans with motors, 2 H.P. exhausters with motors, 1 crane.

3. <u>Winkler Water Gas & Fuel Gas Plant:</u>

5 Winkler generators each 3.7 m ins. dia. 5 waste heat boilers, multiclone, receivers (Verlagen), washer, disintegrators, drip pan, cooler, clarification basin, stack cooler, blowers, motors.

4. <u>Desulfuring Unit for the H_2-poor Winkler Water Gas:</u>

10 adsorbers each 3.4 m ins. dia, 3 gas blowers with motors, 4 containers for wash liquor, pumps with motors, complete sulfur recovery unit.

5. <u>Linde-Fränkl O_2-Plant:</u>

5 separating apparatus, 3 turbo-compressors, 3 booster air compressors, 2 cranes, wash towers.

6. <u>Conversion Unit:</u>

15 catalyst systems each 3.2 m ins. dia. x 15.5 m high, 2 evaporators, 2 coolers, 6 pumps with motors, 4 heating furnaces, jib and traveling cranes.

7. <u>Compressor Unit:</u>

9 6-stage H.P. gas compressors @ 325 atm, 9 synchronous motors each 4000 KW, 9 starters with accessories, 6 booster compressors 300-700 atm, 6 synchronous motors with starters, 4 coolers, 4 separators, 1-30 t crane, 1 - 25 t crane.

8. <u>Pressure Water Wash for Removing CO_2:</u>

8 washers 2100 mm dia, 6 impulse (Freistrahl) turbines, 8 centrifugal pumps, gas separator, 2 wash water cooling towers, 4 CO_2-blowers, 4 raw water pumps with drives and starters, 4 pure water pumps with drives and starters.

9. <u>H.P. Wash Unit for Removing CO:</u>

5 H.P. washers, 9 separators, 3 expansion machines, 4 press pumps with drives, 3 supply pumps, 4 vacuum pumps, various expansion containers.

10. Gas Tanks:

Winkler O-water gas	16000 m^3
Winkler fuel gas	20000 m^3
Catalyst gas	40000 m^3
Return gas	2000 m^3
N_2	2000 m^3
O_2	5000 m^3
Hydrogenation off-gas	5000 "
" waste gas	3000 "
" " "	2000 "
H_2S	500 "

11. Pipe Lines, within buildings.
Measuring Instruments.
Electrical Installations.
Buildings, including steel structures.
Contingencies.

12. Connecting Lines, between the several units of the plant.

IV. Power Production.

To supply the various departments with the required electric power, steam and water, a power plant with boiler house, power house, switch gear and a water works is proposed. In the layout of the power producing units, the steam production in the waste heat boilers of the gas plant, as well as an adequate reserve for peak loads and repair periods, has been taken into consideration.

a. Power Plant.

The boilers have been designed for an operating pressure of 80 atm, a temperature of 500° C, and a total steam production of 590 t/h, one of the 7 boilers being considered a spare. The boilers are powdered coal fired and provided with exhaust draft fans and breeching to a common brick stack. The boiler water is mostly condensate from the feed water heaters and the turbine condensers. The added feed water is chemically treated. The feed water is heated in stages; first by the exhaust steam from the feed pump turbines to abt. 100° C, then in a receiver to 150° C and finally by 20 atm. steam in a surface preheater to 185° C.

The process steam required, 35 t/h @ 20 atm and 150 t/h @ 3.5 atm, is taken from the turbines. The turbo-generators have a rated capacity of 100500 KW, 6000 V, 50 cycle, considering 5000 KW consumed in the power plant itself, a reserve for peak loads, and abt. 84000 KW normally supplied to the plant, of which abt. half each is back pressure and condensation.

The Power Plant includes the following departments:

1. Boiler House.

7 boilers @ 84 t/h/80 atm/500° C, coal bunkers, coal handling, ash disposal, coal pulverizing, 7 exhaust draft units, feed water pumps and heater, pipe lines, measuring instruments, regulators, electric lines, transformers.

2. Power House.

5 bleeder (Entnahme) turbines 70/5/0.05 atm @ 12500/15000 KW, 2 auxiliary (Vorschalt) turbines 70/20 atm @ 12500 KW, 2 back pressure turbines 20/5 atm @ 6500 KW, including generators, steam lines, electric lines, traveling crane.

3. Switch Gear and office.

4. Water Purification.

5. Work Shop.

6. Water Works.

The water supply is designed for 26000 m^3/h and an operating pressure of 5 atm, assuming a normal consumption of 19000 to 20000 m^3/h @ 15° C and a 30% reserve.

V. General and Auxiliary Installations.

a. Power Distribution.

1. Cable system, incl. substation.
2. Steam lines.
3. Condensate lines.
4. Water lines.
5. Gas lines.
6. Compressed air lines.

b. Auxiliary Installations.

1. Administration building.
2. Laboratory.
3. Repair shop.
4. Warehouse.
5. Phenol-& waste water cleaning.
6. Dephenolizing unit.
7. Roads.
8. Sewers.
9. Pipe-bridges.
10. Vehicles, trucks, cars, etc.
11. Tracks.
12. Road lighting.
13. Telephones & signals.
14. Construction bldgs. & installations.
15. Change - and wash rooms.
16. Fire and gas protection installations.
17. Fences.

The extent of auxiliary installations is dependent upon conditions at the site and the requirements of the various departments. The costs for these mentioned herein are, therefore independent of possible increases because of conditions unknown to us.

VI. General arrangement.

(Drawings not reproduced)

The area required for the proposed plant is about 90 ha (abt. 222 acres) which allows for limited expansion. (They didn't know the location of the plant and their layouts are, therefore, based on theoretical assumption).

VII. Prices and Weights.

Material Supplied by Germany.

The bid includes the furnishing of all equipment for the hydrogenation proper and gas production for the total sum of

RM 105,700,000.00 and

RM 46,300,000.00

for the power plant and auxiliary installations. These prices include overseas packing and are f.o.b. Lübeck or Stettin. They also include the catalyst required to start up the plant and a sum deemed necessary for the essential coal tests.

The net weight of this equipment is about 90,000 tons.

The cost of overall planning is figured at RM 5,300,000.00. which includes general drawings required for bids. No detail drawings, calculations of stresses or soil tests are included.

SUMMARY OF PRICES AND WEIGHTS

		RM	Tons
1.	**Gasoline Plant**		
	1. Coal crushing & mashing	4,400,000	2,800
	2. Stalls	30,000,000	12,900
	3. Machine house install.	11,000,000	5,300
	4. Residue processing	5,700,000	2,800
	5. Distillation & Tankage	8,000,000	4,400
	6. Misc. outside lines, gas protection, etc.	6,600,000	4,500
		65,700,000	32,700
2.	**Gas Plant.**		
	1. Hygas splitting, desulfuring & conversion.	14,000,000	7,700
	2. Winkler water-and fuel gas plant, incl. O_2 -production	10,500,000	5,300
	3. Compressors	7,300,000	2,600
	4. Gas cleaning of CO & CO_2	5,700,000	3,300
	5. Gas tanks	1,000,000	2,500
	6. Misc. - pipe lines, etc.	1,500,000	1,500
		40,000,000	22,900
3.	**Power Production.**		
	1. Power Plant	28,800,000	21,800
	2. Water Works	1,200,000	1,700
		30,000,000	23,500
4.	**General & Auxiliaries.**		
	1. Power distribution	7,800,000	3,300
	2. Other auxiliaries	8,500,000	7,600
		16,500,000	10,900

Estimate of Steel required for Bldgs., Fdts., etc. and furnished either by Germany or Russia, based on German conditions:

	RM	Tons
Gasoline Plant	4,100,000	11,800
Gas production	2,600,000	7,800
Power "	900,000	3,100
General & aux.	2,400,000	7,300
	10,000,000	30,000

Furnished by Russia.

Erection of Bldgs.

Other construction work.

Foundations.

Insulations.

Painting

Installing all equipment.

The costs of these items are estimated for similar structures in Germany and amount to:

	Foundations RM	Masonry and Earthwork RM	Installation RM	Total RM
Gasoline Plant	2,300,000	3,240,000	10,340,000	15,880,000
Gas production	1,950,000	2,620,000	6,130,000	10,700,000
Power "	1,550,000	2,690,000	3,030,000	7,270,000
General & Aux.	2,100,000	7,800,000	4,050,000	13,950,000
Total	7,900,000,	16,350,000	23,550,000	47,800,000

No allowance is made for spare parts.

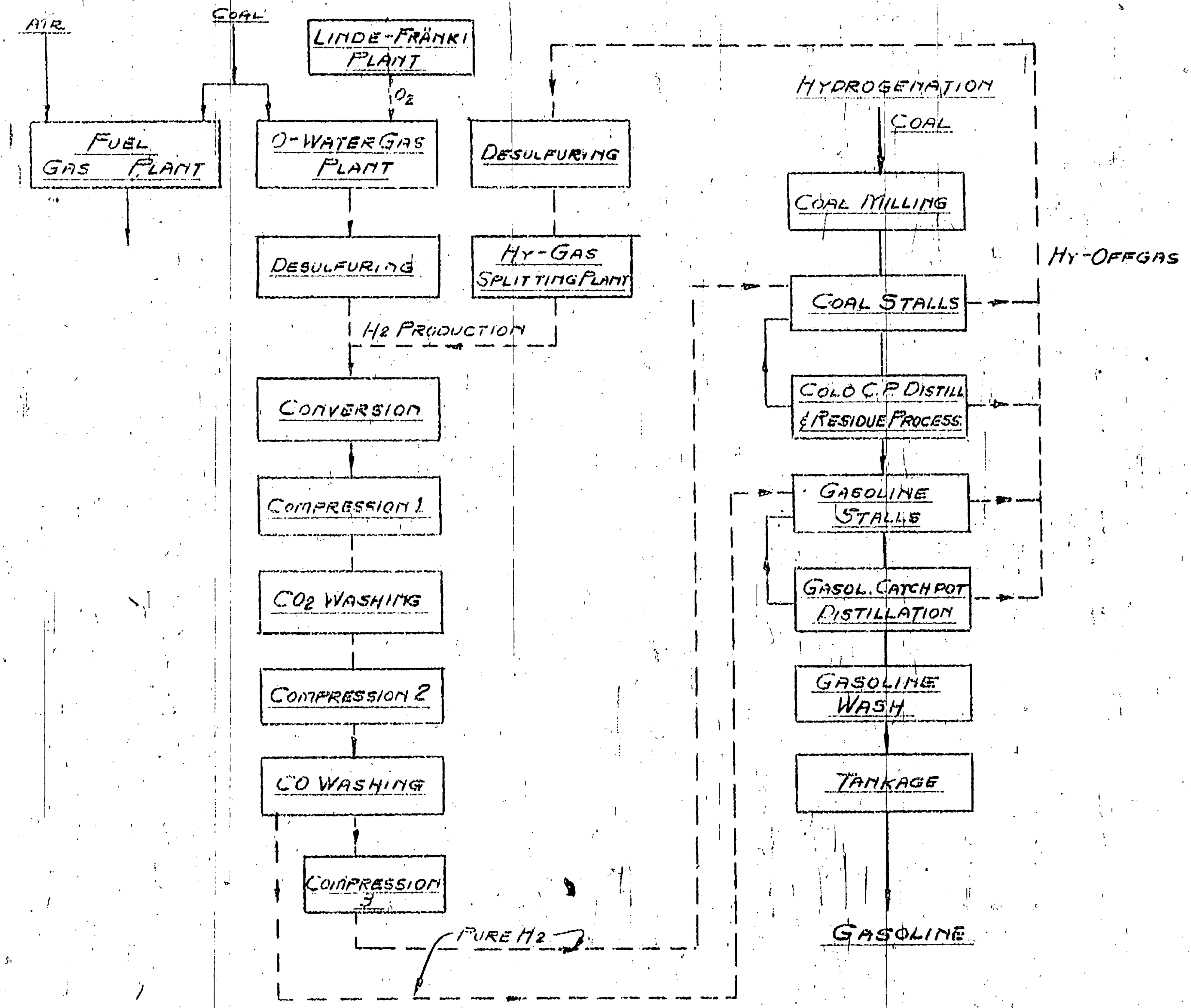
VIII. Conditions of Payment & Delivery

Covers method of payment and delivery agreed upon in detail.

IX. Consumption Figures.

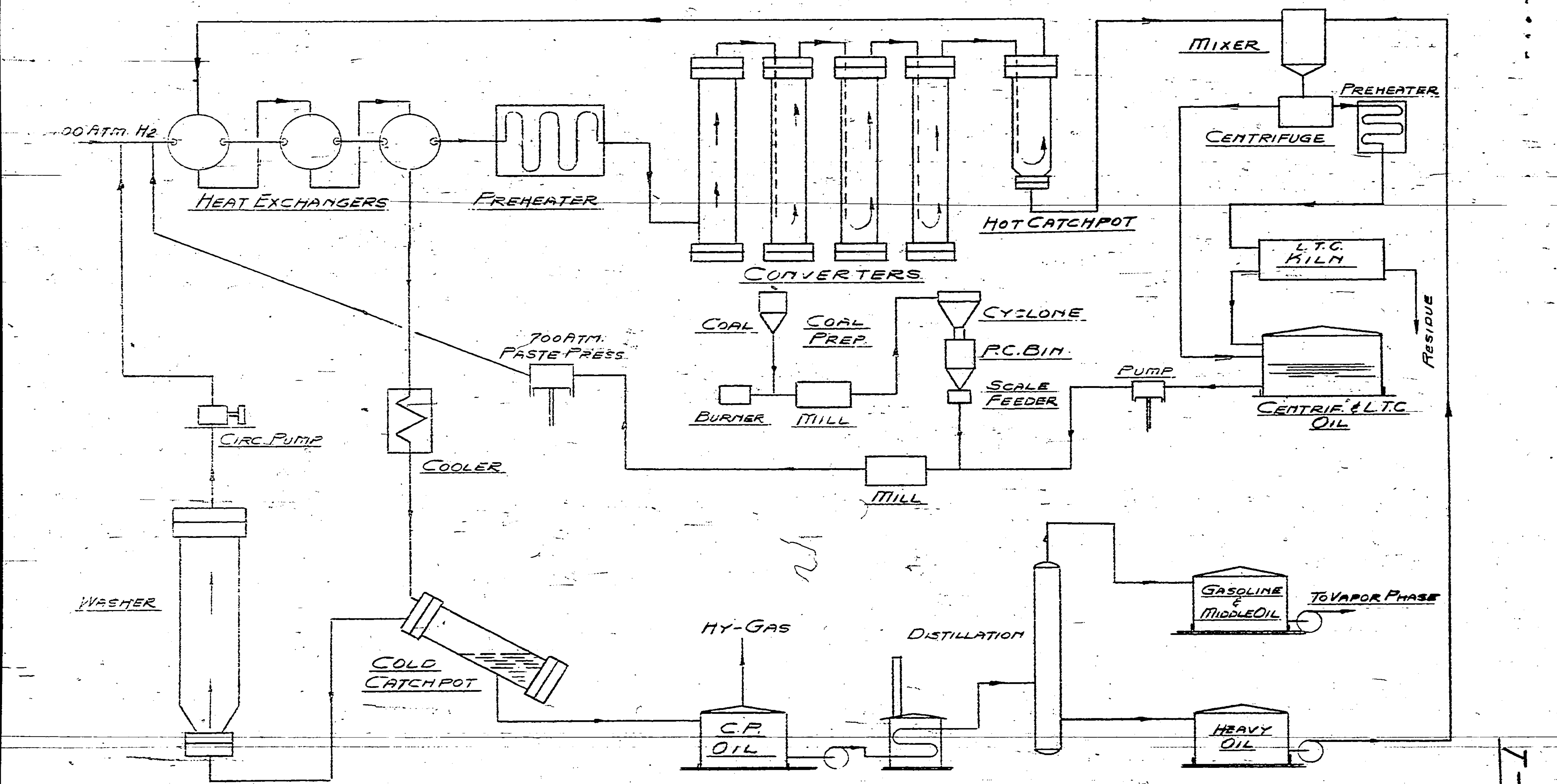
Covers a summary of the figures previously mentioned herein.

The personnel required under German conditions is estimated to be 2500 men, divided into 3 shifts.



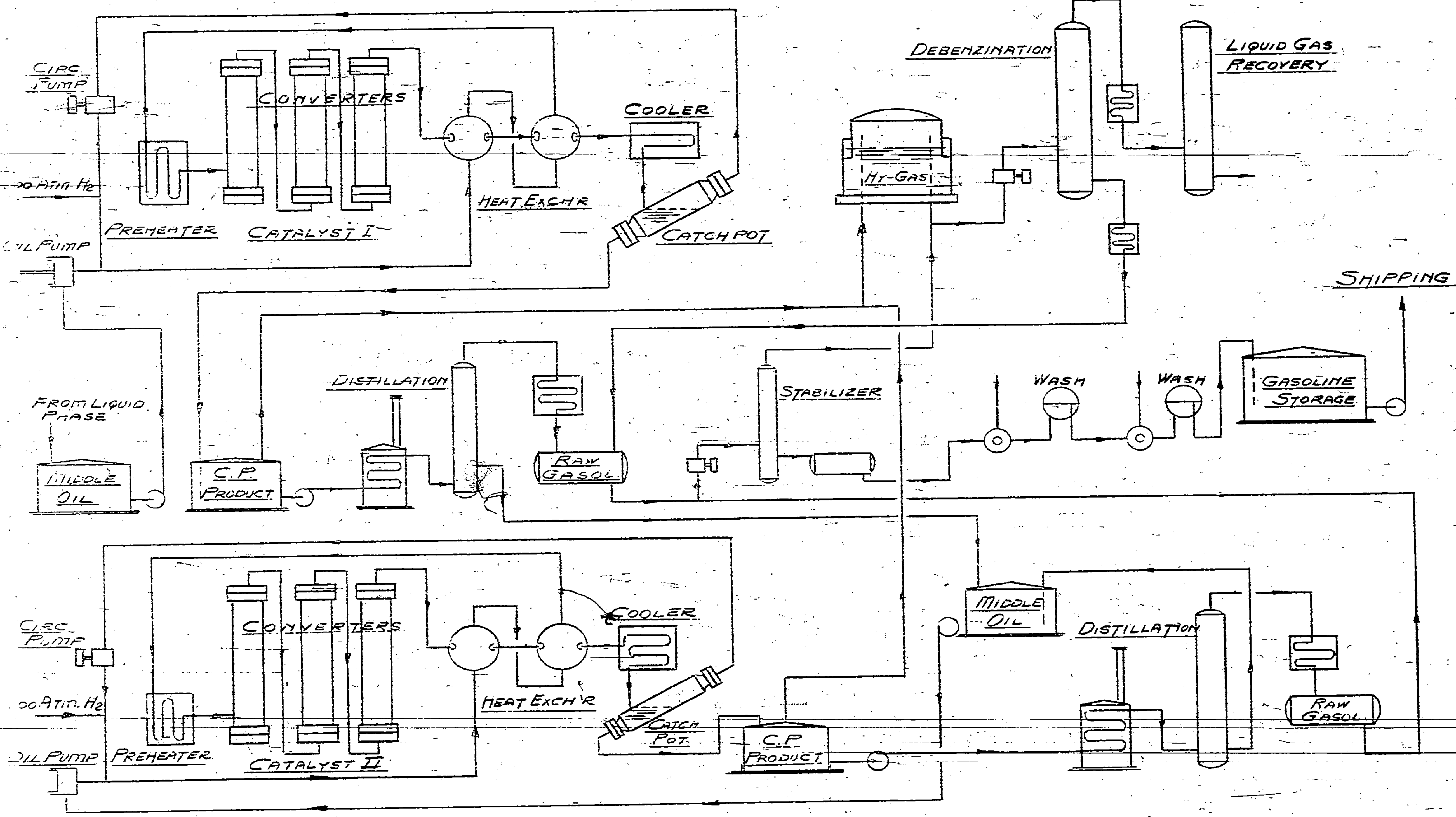
FLOW SHEET OF GASOLINE PLANT

FIG. 1



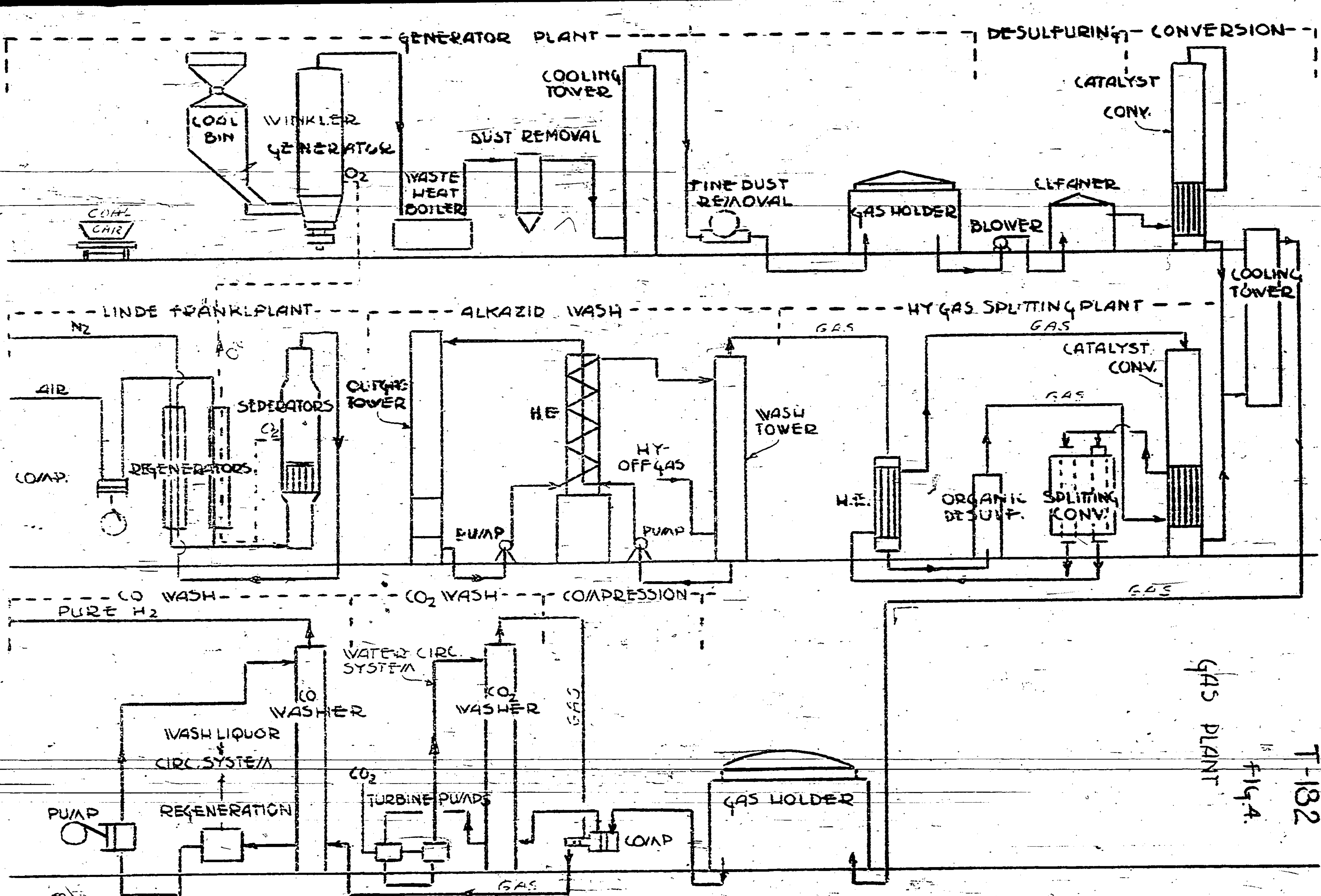
CATALYTIC COAL HYDROGENATION
(LIQUID PHASE) FIG. 2

T-182



Catalytic Coal Hydrogenation (Vapor Phase)
Fig 3.

T-182



GAS PLANT

FIG. 4.

T-132

TOM Reel 130
Ref. t,
Pps. 386-402.

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-183

Feb. 22, 1939
Merseburg,

CHLORINE IN THE VAPOR PHASE INJECTION FEED, ITS REMOVAL AND GENERAL ORIENTATION IN THE OPERATION DETAILS AT HIGH PRESSURE IN SCHOLVEN.

Leuna, 1939.

1). The Chlorine Content of the Vapor Phase Feed and the Removal of Chlorine.

The present chlorine content of the vapor phase injection feed in Scholven is 20 - 30 mg/li.

Chlorine is determined as follows: 50 mls middle oil are burned in a quartz boat in a quartz vessel with H_2. The vapors are absorbed in a solution of bisulfite, and the chlorine is determined in it gravimetrically as AgCl. A nephelometric method had at an earlier data been developed in Ludwigshafen, but has failed, however, to give good results. It has been agreed to exchange samples with Scholven, and to have them analyzed in Leuna as well as in Scholven, in order to test the results.

The chlorine content in Scholven was formerly three times as high as today because: 1) the time the soda solution stayed in the last converter of the liquid phase was insufficiently long to neutralize NH_4Cl. The introduction of the soda neutralization vessel in front of the hot catchpot has improved the neutralization. 2). The Rüttgers oils which were formerly used as outside oils contained 100 mg Cl/li, while their chlorine content has at present also been reduced to 20 mg/li; moreover, the proportion of these oils in the production amounts to only 6% today, against the 12 - 15% formerly.

Chlorine is removed from the vapor phase by injecting 800 li/hr of condensate into the heat exchanger I against the bottom base of the tubes. The condensate is obtained from the 3 atm collector pipe line and is first filtered through a gravel sand filter. The water was formerly led through a felt column filter, but this is no longer done, because sand removes all the impurities. The water was formerly injected against the upper pipe header as is done here. However, dismantling the heat exchangers has shown, that small amount of sand crusts were already formed at the bottom tube header of the exchange I and in the connecting pipe line between I and II, and these crusts consisted principally of NH_4Cl; the water injection was then transfered to the bottom of the exchanger I. An alalysis of such deposits in the bottom tube head of exchanger I gave the following information: water solubles 72%, (which consisted of 9.8% Na, 14.5% NH_4, 42.3% Cl, 5.1% CO_2, Ca and Fe, - traces, some FeS was present). This was the only analysis made during the dismantling of the inside bundle. Formerly, prior to the installation of the neutralization vessel, 800 li/hr of a dilute soda solution (0.04 - 0.07%) was introduced into the feed of the A stall at the bottom of the exchanger I. In addition, twice a week, this injection was increased to 5 m^3/hr; this is however no more required with the low Cl content of the injection feed.

According to Dr. Urban and Dr. Schmidt, no difficulties have as yet ever been caused by high resistance on the suction side of the heat exchangers, nor has any corrosion by NH_4Cl has been observed, but there was a strong deterioration on the pressure side of the exchangers through impurities introduced with the injection feed. For this reason, all injection feed of the vapor phase has been filtered since 1938. Ceramic column filters about 1 m in length are used. The filters are always installed in parallel, and they offer practically no resistance. The reserve filter is put in use every 16 - 20 hours, the used filter is opened, the felt removed and washed. The stones are washed out from the inside to the outside with water from a special washing unit. The felt is freed from water in a wringer similar to those on washing machines, and the filter reassembled. The residue on the filter is principally composed of arsenic sulfide, because the middle oils are sulfurized with Taylor sulfur. There is in addition some rust, iron sulfide, and mechanical impurities. In addition, the felt cloth soaks up some water. The whole filter installation presents an impression of being extraordinarily good, and practical. Leuna is at present experimentally installing a similar filter.

Sulfurizing the A and B middle oils.

The sulfur content of coal is around 1%, while the Leuna brown coal contains about 5% S. The 5058 catalyst loses therefore its efficiency in Scholven, unless the middle oil is sulfurized.

Sulfurizing is done in a tower with sulfur briquettes prepared by the Tylox method, and the method of operation is the same as the one formerly used by us.

0.3% S is dissolved during sulfurizing in the A middle oil,

0.5 - 0.7% S is dissolved in the B + C middle oil.

Scholven is going, however, to omit this kind of sulfurizing, and sulfurize by means of liquid H_2S. This will enable Dr. Urban to activate converter I by separate injection ~~independently~~ of the injection of the 5058 catalyst. Operating conditions in Leuna and Scholven are compared in the table below:

	SCHOLVEN	LEUNA Stall with four 800 mm converters	LEUNA Stall with three 1200 mm converters.
1. Stall equipment:			
2 heat exchang.	600 mm, 18 m. long Sections: I 27 II 30	500 mm, 18 m long Section: 29.5	500 mm, 18 m. long Section: 29.5
	Heat. Surface I-285 m^2, II 228m^2	Heat. surface, 145 m^2 each	Heat. surface 145 m^2 each
Converters:	1000 mm, 18 m. long two converters with blends	800 mm, 18 m long 4 conv. I & II with blends, III and IV no blends	1200 mm, I w. 4 blends, II and III with 3 blends each
catal. vol.	16.4 m^3	20.52 m^3	20.05 m^3
direction of flow	from above in all	from below in all	from below in all
diam. of pipe line between converters	120 mm	120 mm	120 mm
2. Load:			
Injection, amount	10 te	14.3 te	21.1 te, nd = 0.880/20°
load	0.62	0.69	1.05
Sp. gr. catchpot	0.854/15°	0.810/20°	0.800/20°
Gas intake	35,000 m^3	20,000 m^3	38,000 m^3
Total cold gas	21,200 "	23,500 "	30,000 "
gas outlet	44,000 "	44,000 "	61,000 "
density, inlet	0.33 kg/m^3	0.23 kg/m^3	0.23 kg/m^3
" outlet	0.35 " "	0.25 " "	0.24 " "
Max.conv.temper.	411° C	392° C	395° C
Inlet temp. suct. side, exch. II	211°	212° (with only 1000 li water in exch.II -260°)	260°
Press., stall inlet	285 atm	233 atm	240 atm
" inlet in suction side of exch. II	276 "	220 "	227.5 / 227.5"
Total resist. of stall	10 "	16 "	17 atm
Resist. of suct. side,exch.II	0.6 "	2.5"	3.5 atm
K value, exch I	250	220	310
" " " II	250	280	320
Days of oper., exch I	216	127	54
" " " " II	216	23	54
Heat of react.kcal/kg of injection	abt 240	abt. 235	abt. 230
3. Analyses:			
Sulfurising of inject.	0.3% S	none	
chlorine content of injection feed	20 mg/li	abt 150 mg/li	
NH_3 in gases in stall intake	50 mg/m^3	50 mg/m^3	50 mg/m^3

(Table, continued)

H_2S in stall intake gas	0.005% by vol.	0.07% by vol.	
H_2S in stall outlet gas	0.011" " "	0.10% " "	
Phenol in injection feed	130 g/li *	100 g/li	
Water injection:			(formerly:
Exch I, bottom suct. side	800 li/hr-	1500 li/hr	
Exch II top suct."		2000 " "	1000 li) 1000 li
gas cooler		** 2000 " "	1000 li) 1000 li
ammonia removal	500 li/hr for total vapor phase		

*Only 80 g/li phenol were found formerly, because of an oily residue remaining upon the solution of sodium hydroxide which contained appreciable amounts of phenol, which were not removed during the determination.

** Through one distributor nipple.

Comparison of the Distribution of Resistances in the 5058 Stall With Thruputs Shown in the Table.

	Scholven	Leuna 4 converters, 800 mm		Leuna 3 conv., 1200 mm*	
Heat Exch. II		0.6		1.0	
" " I	3.0	0.6	1.7	1.1	3.7
Preheater		0.5		1.6	
Converter I	3.7	1.2		1.8	
" II		2.0		1.1	4.7
" III		1.9	7.8	1.8	
" IV		2.7			
Exch. I		1.6		2.3	
" II	2.0	2.5	4.8	3.3	7.2
Gas cooler	-	0.7		1.6	
Catchpot		0.6		1.1	
Total	8.7	14.9		16.7	

* Extrapolated, because no determinations were made with this thruput.

The following were the reasons why pressure did not rise in Scholven through deposition of NH_4Cl and FeS on the suction side of the cold heat exchanger:

1) the much smaller Cl content of the injection feed of the A middle oil stall, amounting to only 1/7 of the Leuna feed.

2) the much lower H_2S content in Scholven, only 1/10 that of Leuna at the stall outlet.

3) The pressure was 50 atm higher, and the water liquefied even at the higher temperature.

After the zink coating of the heat exchanger tubes in Leuna has been destroyed by the action of Cl, the considerably higher H_2S content causes strong deposition of FeS, which can then be no longer removed with water.

2) Equipment.

The present installation consists of:

Coal stalls: 3 in use, one in reserve, 1 in construction,

two-5058 stalls

two-6434 stalls

The converter service boards are located in the center of the service room. The stalls are operated by two men, one on converter I and II, the second on conv. III and preheater.

The stalls operate extraordinarily **smoothly**, both the liquid and vapor phase stalls.

Single measurements of cold gas are not entered into the converter log, only the intake and outlet measurements are recorded.

The catchpot level attendant and the circulation operators sit on stools.

The flow of the 5058 stall is from above downward throughout, except one stall in which only the last converter is connected in this way. This also, however, is going to be changed. Measurement are made only at a central thermal nippel, none on side nipples, the construction of the old blends is the same as ours, in the converters upward flow. The extraordinarily small number of valves in the new stalls is striking, i.g. the cold gas has only one valve, 16 mm diameter with 5 mm by-pass. In the future Dr. Urban will operate entirely without by-passes, and put in only one 10 mm valve. All the old cold gas measurements will be omitted, and only a single total measurement made. Leuna can not consider such simplification, because when a stall is started up, 30,000 m^3 of additional cold gas is introduced gradually. All the throttling valves are placed in horizontal lengths of pipe, the cold gas pipe line goes to the stall at an elevation of about 2 m. Both heat exchangers can be let down, while in Leuna only the cold heat exchanger: we consider the let-down of the hot heat exchanger being superfluous.

Liquid Phase Stall. The injection, temperature distribution and amounts of gas are shown in the sketch. (Omitted from the report)

The extraordinarily steady operations of the stall are surprising; it is to be attributed to the fact, that Scholven operates with no paste heat exchange and with no HOLD heat exchange. Variations in the amount of HOLD can therefore only be noted in the gas passing through heat exchangers. The large preheater buffers these variations to a large extent. In Leuna, variations in the HOLD production because of the large degree of heat exchange of the products will be carried over to:

1. The paste mixture passing through the heat exchanger.

2. The gas of the HOLD heat exchange, which in turn produces variations of 5 to 15 mv in the course of ¼ hour in the gas-paste exchanger.

3. The gas of heat exchanging of the intermediate catchpot which is added in a separate horizontal heating unit in the cold pass of the preheater immediately in front of converter I, and may directly affect the temperature in the converter by variations in its temp

The amounts of gas in these locations are as follows in Leuna:

1.	Cold gas to exchanger II:	15% of the total gas intake
2.	Gas for the HOLD heat exchange and the cold coil of the intermediate catchpot to heat exchanger II	40-50% " " " " "
3.	Gas from the intermediate catchpot heat exchanger to preheater section of converter I	25-35% " " " " "

No regulation whatsoever is done on the gas preheater, one man is detailed every two hours to check the preheater operations. The heating value is very constant, 4300-4800 h.u. The gas preheater is always operated to full capacity, all the suction and pressure valves are fully open.

There are 3 paste presses to each stall, two for paste, the third for pasting oil, to permit an immediate changing over to pasting oil in case of trouble. The same paste presses may not be used for any stall, each stall has its own three presses.

<u>Calculating the Operating Time of a Coal Stall.</u> The longest operating time of 290 days has been given. Dr. Urban figures the true injection time as the operating time, during which the gas preheater feed, the converters and the HOLD were used. Alterations could be made on all the other parts of the equipment, e.g. closing gaskets or heat exchangers could be changed. In one old report of 1938 even a converter was changed and the operating time was counted continuously. The gas preheater feed is the most important, and computations are made on the strength of it.

<u>Starting up a Coal Stall.</u> Heating with gas to 8 - 9 mv, then injection of 4 te/hr of solid-free flushing oil (distillation heavy oil) up to 11 - 12 mv, next of 15 te/hr of pasting oil, using the hot pass of the preheater.

Changed over to coal paste at 20 - 21 mv and preliminary operation with 29 te/hr of the four converter stalls and 23 te/hr of the three converter stalls. At the start of the change to coal the hot circuit is changed over to the hot catchpot. The speed of heating up is 1 - 1.5 mv/hr. Scholven is apprehensive while heating with gas, only about the drying out of the oil residues in the preheater and the heat exchanger; for this reason oil is already introduced at 8 mv. Pasting oil may not be used before 12 mv, because of its 10% solids and 12% asphalt content it foams at lower temperature in the cold catchpot and the hot catchpot. The temperature of the coal catchpot is kept at 50 - 60°; the catchpot foams at lower temperatures. The circulation gas is cooled with water from 50 to 30° before entering the scrubber, and the condensate is removed through a catchpot.

<u>Gas Preheater of a Coal Stall.</u> (Separated burners) operate exceptionally smoothly and are operated at full capacity. There are no collector valves at all on many stalls on the suction and the pressure sides, because of the high pressure losses caused by them (e.g, the pressure side valves - 30 mm). The blower may be started without these valves, with only the distributor valves present on the suction and pressure sides. Current consumption during starting 37 amp. (the relay is set for 40 amp.).

Schiele's blower # 1160 can not operate in Scholven without a collector valve, but the Schiele blower #1162 can, because of its higher capacity which percentually reduces the leaks. This fact must be considered in connection with the exceptional tightness of the preheater. The peepholes at the burners are also provided with valves when in use.

Method of Starting. Suction valves are opened, pressure valves closed, the exhaust valve closed. No regulation is actually done on the preheater. The heating value is very constant. O_2 exhausted about 2%.

Scholven claims the low temperature of their burners as one of their main advantages, because it permits more rapid cooling than our large combustion chamber.

The temperature difference over the height of the preheater in the cold pass amounts to 270 - 330°. We show for comparison one of our Leuna preheater (v. table). The temperature distribution is therefore no better in Scholven than in Leuna.

In my opinion, Scholven can operate with the preheater only because

1. The heating value is very constant;

2. The preheater is fully utilized during the starting as well all during operations, while our preheater operate ordinarily at only 1/3 their capacity, but must for a short time be operated at full capacity during starting.

3. The stalls are regulated hardly at all and operate very uniformly.

While the stall was idle, an Escher Wyss blower was used experimentally with cold gas; it is supposed to have an efficiency of 80% (Schiele blower - 60%).

Energy consumption with 250,000 m^3 gas (400° C), with 300 mm compression - 300 kw. The wings are adjustable, the construction very small and space conserving. The elbows at the blower at the drive are omitted.

No operating experience is as yet available.

Materials. 1. All heat exchangers have stuffing box lubrication, which are serviced in operation. This has not so far been missed in Leuna.

2. The horizontal circulation gas pumps have ring packing, which have been found very satisfactory. Operating life about 1 year.

The rods are of not-nitrided Mannesmann steel. Depth hardened steel, Brinell hardness 500 - 600.

3. Middle oil injection pumps: 3 Balcke plunger pumps, 35 cm stroke, 105 rpm, 70 mm diameter of plunger have performed well with sulfurized injection feed, flushing oil is also run with them. With the Götze C_1 packing 12,000 hrs have been reached with flushing oil.

The Burgmann cord is used by preference with the middle oil pumps, but it is less satisfactory than Götze C_1 with sulfured feed. Scholven has no more trouble with valves, since the injection feed has been filtered. Stuffing boxes have no flushing oil connections. The Götze packing is now again being introduced.

4. Paste Presses: Max. capacity 25 m^3/hr. Stuffing boxes: U sleeve packing of lead bronze Te Go 3 (Goldschmidt) is satisfactory, abt 3000 hrs operating life. White metal can not be used because the temperature is too high (120-130°). 200 li/hr per pump of flushing oil. Welheim also uses lead bronze, but the next harder kind.

Piston rods: Mannesmann Verbundstahl, outlast 3 - 4 changes of packing, and are then rehardened.

5. Return Compression. Only in the vapor phase.

The exhaust gas 300 -- 110 atm is returned for recompression. It contains 60 - 70% H_2 and is compressed directly with a two-stage compressor in the pressure side of the gas circulation.

1-st step 100--170 atm.
2-nd step 170-300 atm.

Return Gas Compressor, Maschinenfabrik Esslingen. Capacity 700 m^3/hr, at 100 atm pressure at the suction side.

Stuffing boxes: Ring packing

Piston rods: Mannesmann Verbundstahl

No trouble, except for the ready breaking of the plate valves.

6. The suction side of the gas circulation pumps is heated to the collector pipe line as protection against condensation.

7. All the surge tanks are placed in the side lines, Scholven does not know where the suggestion comes from to place the surge tanks of the new installations into the main line.

8. The new preheater to be erected is built for 6 million useful heat, and is composed of 18-120 mm hairpins, and
9-90 mm hairpins.

9. The H_2S content of the fuel gas if 1.5 g/m^3; no formation of $FeSO_4$ has been observed.

10. The flue of the suction side of the preheater acts also as an explosion safeguard.

11. Valves for rapid HOLD.

These were erroneously given in the drawing of the letter of 11/25/38 throttling valves which can not be used, because their free cross section is too small.

12. Check valves are absolutely necessary on the cold gas pipe line, because with the frequent changes in the flow, the paste will immediately coke in the cold gas pipe line.

13. An air cooler is installed in the coal stall between the heat exchanger and the gas cooler to reduce corrosion. It has a distributor in the inlet made of a V 16 A tube.

14. Ball kilns. Injection 2.5 ts/hr of centrifuge residue.

Both kilns are in operation since January, one of them was shut down a few days ago to strengthen the worn parts. The injection feed contains 12% asphalt and 25% solids. The filling material has not yet been put in.

/s/ Kimmerle

W. M. Sternberg
12-11-46

STALL 9. 6434 Catalyst, Nine Operating Days (with gas preheater)

3 converters, each with 6 blends, flow from above downwards, old blend construction, cold gas (1000 mm diameter) Introduced through lid.

<u>Temperatures.</u> Heat exchanger, outlet pressure side,	19.7 mv	Gaspreheater inlet		19.8 mv
Converter I	21.4-21.6 "	" "	outlet	21.6 "
" II	21.8-21.6	Fuel gas consumpt.		380 m^3 (4700 h.u.
" III	21.5-21.7	Temperature 30° at cold junction		

<u>Thruput:</u> 20 to/h, sp.gr. 0.880/15° injection, the feed contains 0.5-0.7% S.

27,000 li HOLD, sp.gr. 0.754/15° (is supposed to contain 75% gasoline)

Gas intake: 30,000 m^3

" outlet: 48,500 m^3

Cold gas:

conv. I	9,700 "	Sp.gr., stall inlet: 0.345
conv. II	6,600 "	" outlet: 0.375
Conv. III	5,500 "	
Total	21,800 "	K values of heat exchangers: exch. I 400 (30-th sect.*)
		" II 200 (27-th ")

*The heat exchanger still has a 30-th section, but will be exchanged and made the same as the rest.

-12-

THRUPUTS THROUGH STALL

	With 3 Convert.	With 4 Converters.
Injection	23,000 kg	29,000 kg
Coal contents of injection	46%	46%
Ash in coal	6.8	6.8
The pasting oil contains:		
% solids	12.0%	12.0%
ash in solids	26.0%	26.0%
In addition, film oil	1000 kg	1500 kg
Solids in film oil	12.0%	12.0%
Ash in film oil solids	26.0	26.0%
HOLD, kg	11,000	14,000
Solids in HOLD	25%	25%
Utilization	92 - 94%	92 - 94%

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

SULFIDIC VAPOR PHASE CATALYSTS, ESPECIALLY TUNGSTEN SULFIDE IN INDUSTRIAL COAL HYDROGENATION

Lecture by M. Pier, Ludwigshafen, 1943

The industrial investigator studying new catalytic processes has at his disposal on the one said the specialized experience gained in the development of similar problems which, supposedly, may be carried over to the new process with a certain intuition. On the other hand, he draws great benefits from the firmly fixed laws of science. The Bunsen Society has frequently reported on the work of industrial chemists in the field of catalysis, e.g., in articles by A. Mittasch and H. Bütefisch.

I will discuss today a chapter on industrial catalysis at the request of the State Office for Industrial Development. As an introduction, I shall briefly tell about the historical development of high pressure processes of the I.G. from ammonia, through methanol and to gasoline, and discuss then the special case of gasoline production with a fixed bed catalyst - tungsten sulfide. I will report on the preparation, properties and uses of this versatile catalyst, but in order not to excite too great expectations will say right at the start that with the stormy development of the process, a condition which still persists, and with the great number of practical problems to be solved, no extensive study of basic facts has as yet been possible.

The hydrogenation of nitrogen is done chiefly with metallic catalysts for which hydrogen sulfide, phosphine and carbon monoxide act as poisons. They are mostly metals of the 8-th group, in particular iron, and a solid catalyst is obtained from fused iron oxide improved or activated by the addition of alumina, alkalies, etc. Molybdenum and tungsten may be used instead of iron but not in the presence of alkalies.

When hydrogen and carbon monoxide are acted upon catalytically, methane is chiefly formed with a catalyst like nickel. When we discovered the hydrogenation of carbon monoxide to methanol under high pressure - just 20 years ago - and used it industrially, we found that at temperatures in excess of 300°C iron as well as other carbonyl forming metals must be avoided when oxygenated substances are desired. Reactions with oxidic catalysts could be carried out only after elimination of iron. Oxides difficult to reduce were tested with hydrogen. A few tests were sufficient to show that at 1,000 atm. methanol alone was actually obtained and zinc oxide-chromium oxide catalyst was developed as the best catalyst, which was then introduced into the ammonia synthesis at the pressure of 200 atm. then used. There exist more active catalysts such as copper chromate, but they are sensitive to sulfur.

The discovery that oxide catalysts used in the synthesis of methanol were less sensitive to sulfur than the metallic catalysts was particularly important. In addition, methanol synthesis is a typical example of directing reactions by means of catalysts. Factually, as well as historically, they form a transition between the ammonia synthesis and the manifold reactions during the hydrogenation of coal.

Changing catalysts and the operating conditions, such as pressure, temperature and the concentration of carbon monoxide, permits conducting the reaction between hydrogen and carbon monoxide along different paths and, like in the hydrogenation of coal, the reaction of formation of methane, of the formation of carbon black, condensation, etc., must be avoided. The production of higher alcohols, in particular isobutanol instead of methanol, is possible at high pressure and somewhat higher temperature by the addition of alkalies to the catalyst. Liquid or even solid hydrocarbons, with no appreciable amounts of oxygen compounds, are obtained at lower pressure and temperature, i.e., at about 200° using metallic catalysts especially cobalt and iron deposited upon carriers. This is the well known Fischer-Tropsch synthesis which is used by the Ruhrchemie on a large scale. The metal catalysts are here again sensitive to catalyst poisons such as sulfur.

Upon the successful solution of the methanol synthesis, Bergius tried in 1924 the splitting hydrogenation of coal, tars and oils which had been discovered before the first World War but it could not be carried out successfully either in the laboratory or on an industrial scale without the use of catalysts. The raw material contained sulfur which has led to the assumption that only such substances could be used as catalysts which are not damaged by sulfur and that sulfur itself might act as a catalyst or possibly be a part of the catalyst. Like in the methanol synthesis study, a simple thought was basic in the development. A few dynamic experiments in the laboratory with molybdenum and tungsten sulfides and oxides were sufficient to transform brown coal tar almost completely into gasoline at low partial pressures of the oil with molybdic acid as a catalyst. Similar results, but with a lower production, were also obtained with the sulfides and oxides of cobalt and with iron sulfide. This simple successful series of experiments was the cause of undertaking the coal hydrogenation on a large scale. After overcoming many difficulties of technical and economic nature, it has led after many years of experimenting to the Leuna-Benzin organization and forms today the basis of our gasoline and oil supply from native coals, tars and oils, especially our production of aviation gasoline. A production in terms of millions of tonnes per annum has been reached under the direction of the State Office of Industrial Development.

Catalysis is the essential part of the development. The catalysts had to direct reactions to the production of the desired finished products such as aviation, motor gasoline or diesel oil, etc., from the different raw materials used. It was necessary to develop catalysts of the greatest possible versatility because different raw materials were to be used in the same installations. Different finished products had to be obtained with the best utilization of the different character of the raw materials, e.g., the aromatic nature of bituminous coals and the paraffinic nature of brown coal tar. In many ways, new catalysts saved the day in several critical instances.

It was found early in the development of the process that it could best be broken up into two steps, the liquid and the vapor phase processes. In the liquid phase process, the high molecular weight raw materials were acted upon. Some of these materials have a tendency to condense upon the catalysts during industrial use with high thru-puts, because with the greatly polymerized aromatic hydrocarbons the hydrogenation equilibrium of hydrogen at temperatures above 450° and at pressures of 200 atm. is still very far removed from the side of the products of hydrogenation. For this reason, today work is frequently carried out in the liquid phase at pressures of 700 atm., using either cheap catalysts or such which can be regenerated. Solid catalysts usually are used in a finely dispersed state.

The readily volatilisable oils, the so-called middle oils, are readily transformed into gasoline in the vapor phase in the presence of fixed bed catalysts at pressures of about 300 atm., occasionally also under 700 at. pressure, and temperatures around 400°. The capacity of one industrial unit is up to 100,000 te. gasoline per annum. Mastery over the heat of the reaction of such a system is an important feature of the problem to permit operating at some uniform temperature. Varying the conditions somewhat, for instance by operating at a lower temperature, the vapor phase hydrogenation may be used in addition to gasoline production also for the purpose of refining and hydrogenation. The first catalysts used were the sulfides and oxides of the metals of the 6-th group. A very important versatile industrial catalyst was molybdenum oxide with additions of magnesium and of zinc oxides, which can also be used at higher temperatures for the production of aromatic gasolines. Tungsten oxide - magnesium oxide has been found suitable for similar purpose.

Middle oils are only partially transformed into gasoline in a single pass over the catalyst. It is important that the remaining so-called middle oils be not converted into too low hydrogen products, as in cracking, and that they do not form a too high proportion of high boiling constituents lest they be less readily split up in the second pass through the reaction chamber. This did not damage the old and more robust catalysts but increased the gasification and reduced the gasoline yield and production efficiency of the process.

A specially prepared tungsten sulfide catalyst has become today an important forward step by proving to be an especially active vapor phase catalyst which operates at lower temperatures than the molybdenum catalysts used formerly, and permits higher thru-puts even with the difficult-to-split oils from bituminous coal. For certain uses, such as the improvement of the anti-knock properties, or the saving in tungsten, it is strongly diluted, i.e., is replaced with other active substances or with carriers, but it still remains a fundamentally important catalyst.

The usual tungsten sulfide is a bluish-black crystalline substance, crystallizing in the hexagonal system, and having a specific gravity of 7.5. It is practically insoluble in any solvent without decomposition. A model of the lattice structure was constructed from X-ray data (not reproduced in this translation). It shows that tungsten sulfide crystallizes with a hexagonal layer lattice with the spacing between the W atoms of 3.18 Å and a spacing between the layers of 6.25 Å. It is isomorphous with molybdenum sulfide which it also resembles in many others of its properties. It does not melt nor decompose appreciably at 1100° C. while there is a strong evolution of sulfur at 1200° C. The usual WS_2 is stable towards hydrogen up to 600° C. At higher temperatures, it is reduced with the formation of hydrogen sulfide.

These data with the ordinary tungsten sulfide were confirmed by Privy Counselor Schenck. His studies on using up sulfur in our tungsten sulfide catalyst are still in progress. There is practically no reduction of it under the conditions of hydrogenation under pressure, as long as the raw materials contain sulfur.

Different methods for the production of tungsten sulfide are known. To obtain a particularly active form of catalyst, a method of preparation must be selected which will result in the formation of a substance with a particularly large surface with an especially large number of active centers. It is also essential to avoid the use of high temperatures. A careful sulfurizing of ammonium tungstate or tungstic acid with hydrogen sulfide comes into consideration. The preparation of tungsten sulfide from ammonium sulfotungstate has become particularly important and results in the preparation of an especially active catalyst when pure raw material is used.

Technically pure tungstic acid anhydrides with less than 0.2% impurities is dissolved at 70° C. in aqueous ammonia or in the mother liquor obtained from previous precipitations containing ammonia and hydrogen sulfide. The filtered solution is treated with an excess of hydrogen sulfide at a slightly raised pressure and at an elevated temperature, which causes ammonium sulfotungstate to begin to crystallize. The temperature is then slowly reduced to 20 - 25° C. while maintaining an excess pressure of hydrogen sulfide to complete the crystallization.

Ammonium sulfotungstate is formed in accordance with the equation:

$$(NH_4)_2WO_4 + 4\ H_2S = (NH_4)_2WS_4 + 4\ H_2O$$

A sufficient excess of hydrogen sulfide will take care of the formation of the less active oxy sulfotungstate:

$$(NH_4)_2WO_4 + 2\ H_2S = (NH_4)_2WO_2S_2 + 2\ H_2O$$

The crystallized sulfosalt is suction-filtered, dried and decomposed in a stream of hydrogen:

$$(NH_4)_2WS_4 + H_2 = WS_2 + H_2S + (NH_4)_2S$$

and cooled in a stream of nitrogen. The decomposition is mostly carried out at temperature of 400° C. However, catalysts decomposed at somewhat lower temperatures are more active for certain purposes. The tungsten sulfide forms a grayish-black crystalline powder with metallic luster. In subsequent operations, air must be most effectively excluded.

To be technically satisfactory, the catalyst must satisfy the requirements of strength, resistance to abrasion, good filling up of space, small resistance to gas in motion, in addition to high and uniform activity, temperature stability and long life. Tungsten sulfide can be readily compressed to tablet form, which satisfy these requirements.

The tableting of powdered tungsten sulfide is done in tableting presses under a pressure of around 5,000 atm. Smaller tablets have a higher specific efficiency, but because of the lower resistance to flow, tablets are usually made 10 mm in diameter and height with about 50% porosity. The table below contains some information on such tablets.

Size of tablets		10 mm diam., 10 mm high
Volume		0.785 mls.
Weight		3.15 g.
Outer surface of tablet		4.7 cm^2
Number of tablets per liter		830
Weight of 1 liter of tablets		2600 g
Surface of tablets		0.39 cm^2
Crushing strength	abt.	300 kg/cm^2
" "	after 1-1/2 yrs. in use	270 " "

Depending on operating conditions, the tungsten sulfide vapor phase catalyst loses so much in activity after 1-1/2 - 2 years of use that a replacement is advisable. Some individual batches have been in use after five years.

Before the introduction into the converter, the tungsten sulfide catalyst usually contains some excess of sulfur as well as small amounts of moisture and sulfuric acid formed because of an imperfect exclusion of the air, principally by oxidation of absorbed hydrogen and of the excess of sulfur. The molar proportion of tungsten and sulfur is not, therefore, absolutely constant in technically produced catalysts. A slight deficiency of sulfur is found occasionally, but in most cases sulfur is present in excess and the molar proportion may reach 1: 2.2.

Tests have shown that the used catalyst differs outwardly very little from the fresh catalyst and its formula corresponds to that of the fresh WS_2. The principal reason for the loss in activity is the partial irreversible coating with high molecular weight low-hydrogen hydrocarbons, mostly the result of condensation. In addition to small amounts of hydrogen, ultimate analysis of used catalyst disclosed, e.g., some 2% carbon.

The catalyst may be reworked in a very simple way after the removal from the converter. It is roasted in air and the roast treated similarly to the tungstic acid.

Pure tungsten sulfide appears to us to be a particularly interesting example of catalysts for heterogeneous catalysis. A consideration of the structural peculiarities of tungsten sulfide, which together with the convenient melting point may be of particular importance for its catalytic action would bring us to the presence of a layered lattice. The favorable lattice spacings and in particular the van der Waals forces inside the large layer spacings may play here a leading role. In addition, the pseudomorphic form of the tungsten sulfide which retains the ammonium sulfotungstate structure, results in a strong loosening up of the finely crystalline structural parts. In this way, a combination of a mosaic-like structure with a large surface development may result in the formation of the catalytically active centers. The excess of the sulfur or tungsten ions at the edges of the large lattice complexes may also exert a beneficial action. The excess sulfur may form temporary active spots and be displaced elastically by the participants of the reactions. Experiments in this direction are still being continued.

A conclusion of probable importance for the catalytic activity may be made from the method of preparation from ammonium sulfotungstate. Ammonium sulfotungstate crystallizes in well developed shallow prismatic monoclinic crystals. The tungsten sulfide produced from it by thermal decomposition displays the same outer crystalline form under a microscope. The crystals have become opaque but their outline may be clearly recognized. One may see a certain contraction and may even observe directly some pores and small cracks through which hydrogen sulfide and ammonia have escaped. We evidently have here a pseudomorphism of WS_2 after ammonium sulfotungstate. This appears to be favorable to catalytic activity through the creation of the finest system of pores accessible from the outside.

The assumption of a favorable effect of pseudomorphism on the catalytic activity is further confirmed by the good catalytic activity of tungsten sulfide obtained by pressure sulfurization of ammonium tungstate, producing a pseudomorph after ammonium tungstate.

X-ray photographs actually show that in spite of the monoclinic crystalline structure of tungsten sulfide it is present in the well known hexagonal structure but extremely finely distributed. Ammonium sulfotungstate forms a Debye-Scherrer image with an extremely large number of lines as one should expect from its lower symmetry but the tungsten sulfide formed out of it first presents a picture with widened lines which must be attributed to the usual tungsten sulfide. This classification is confirmed by heating the sulfide to higher temperatures, when the photograph will represent the regular sulfide. The apparently different line distribution in the photograph of the heated sulfide as shown in the original paper (and not reproduced here) is caused by changes in intensity probably brought about by a mechanical orientation of the lamellar sample.

On the other hand, amorphous tungsten sulfide is formed by maintaining an especially low temperature (250° C.) during the thermal decomposition, while the industrially-produced catalyst has lines of moderate width which merely become sharper after years of use. This indicates that the loss in catalytic activity during operation can by no means be attributed only to an increase in size of the crystals.

The widening of lines of the active catalyst may be caused by a reduction in size of the crystals as well as by changes in the lattice structure. Tungsten sulfide forms a layer lattice similar to graphite and one should anticipate the formation of lamellar primary particles. Were the widening of the lines explained by size reduction, the average thickness of the lamellae would figure to 3×10^{-7}, corresponding to about 5 - 6 layers of tungsten sulfide, while the catalyst recrystallized by heating would be composed of particles of about twice that thickness. The width of the lamellae should be greater than the thickness. Lattice changes are also present and they seem to form because the individual layers of tungsten sulfide are not located exactly above each other. These changes may also be of importance for the catalytic action.

Electron diffraction has also been used in the investigation of the catalysts. The results so far obtained for pure WS_2 do not as yet agree with the results of X-ray measurements, but some interesting results obtained with mixed heavy metal sulfides should be mentioned. Electron diffraction photographs of the fresh catalysts showed only lines of the mixed components, but catalysts used for some longer time had in addition the lines of the addition compounds. X-ray investigations showed no difference between the fresh and used catalysts.

For a technical man, investigations such as X-ray are merely means to further the development of catalytic processes. The values communicated must not therefore be considered as complete investigations, but rather as orienting measurements which are to be continued. This may be even more strongly so in the absorption measurements and for the hydrogenation experiments with uniform raw materials.

Adsorption measurements with an inert gas, argon, gave the specific surface of the catalysts. Adsorption measurements are difficult with tungsten sulfide because of the difficulties of obtaining a clean tungsten sulfide surface, uncontaminated with sulfur, sulfuric acid, etc. The values obtained are therefore to a certain degree uncertain.

With 50 m^2 surface per milliliter of space filled with catalyst, tungsten sulfide belongs to the surface active substances such as activated carbon or silica gel, and has a much greater surface than the substances normally called porous, such as pumice. The inner surface of the tungsten sulfide catalyst is over one hundred times larger than the outer surface of the tablets. The size of this surface leads to an estimate of the particle size which is somewhat larger than the primary particle size given by X-ray methods.

SPECIFIC SURFACES OF DIFFERENT CATALYSTS

Surfact of catalyst	m^2/g catalyst	m^2/ml catalyst space
Activated charcoal	400	150
Silica gel	110	50
Active WS_2 (from the sulfosalt)	20	50
Pumice	1	0.5

The heat of adsorption of tungsten sulfide obtained from the adsorption isotherm with argon was 2500 - 3500 cal/mol. This indicates but a very slight adsorption action, as one would naturally expect with one of the inert gases, and also that the amounts adsorbed actually are a measure of surface, as has been assumed in the calculation of the surface.

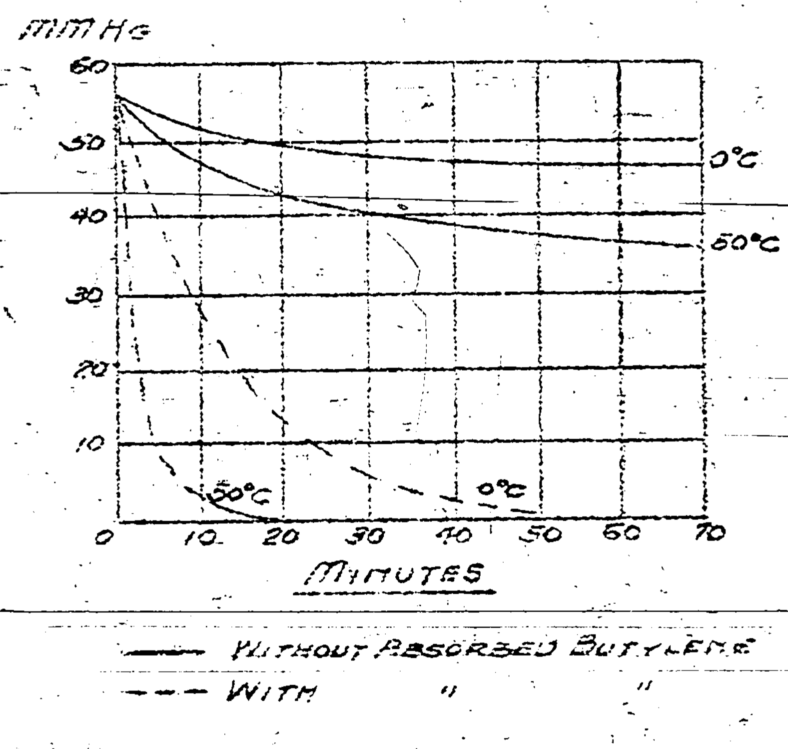
Should less inert gases than argon be used in adsorption experiments, e.g. hydrocarbons, the selective nature of adsorption comes into evidence. The table below shows a few values culled from a number of adsorption isotherms determined for activated carbon, silica gel and tungsten sulfide. At the same pressure of 5 mm Hg., silica gel adsorbs at 0°C. twenty times as much ethane as of argon and fifty times as much ethylene. Carbon adsorbs 130 times more ethane and approximately the same amount of ethylene, tungsten sulfide 160 times more ethane and about 600 times more ethylene, i.e. tungsten sulfide possesses a strong specific adsorption of hydrocarbons, and preferentially the unsaturated ethylene.

GAS ADSORPTION WITH DIFFERENT CATALYSTS

mls adsorbed gas per ml catalyst	Argon	Ethylene	Ethane	Hydrogen
Activated carbon	0.02 (100)	2.7 (100)	2.6 (100)	0.02 (100)
Silica gel	0.005 (25)	0.25 (9)	0.1 (4)	0.02 (100)
Active tungsten sulfide (from the sulfosalt)	0.013 (65)	7.8 (290)	2.1 (80)	0.55 (2700)

This selective adsorption of unsaturated hydrocarbons and of hydrogen by tungsten sulfide is an activated adsorption, i.e. at the same pressure, but somewhat higher temperature, e.g. 50°C., even more ethylene, butylene or hydrogen is adsorbed than at lower temperature, which is the opposite to the way argon acts. One might be tempted to predict from these data that tungsten sulfide is a good catalyst for hydrogenation, but adsorption measurements alone are insufficient to draw conclusions on the suitability of a catalyst for pressure hydrogenation.

As a first step in judging the activity of a catalyst, one must take into consideration the rate of adsorption as well as the amount adsorbed. This process occasionally determines the course of catalytic reactions. The curves below show the rate of adsorption of hydrogen by tungsten sulfide (the two upper curves). If an amount of butylene corresponding to the amount of hydrogen to be used be adsorbed in the apparatus before the introduction of hydrogen, the adsorption of hydrogen will proceed more rapidly, along the two bottom lines, because the unsaturated hydrocarbon upon the surface of the catalyst will rapidly consume hydrogen.



VELOCITY OF ABSORPTION OF H2 ON TUNGSTEN SULFIDE

It may be mentioned in conclusion that the rate of adsorption upon a catalyst which has become inactivated through long use is very greatly reduced.

The reactions in the adsorption layer just described proceed very slowly at room temperature. Tungsten sulfide catalyst accelerates however extraordinarily another reaction, namely the detonation of hydrogen-oxygen mixture even at room temperature, but the catalyst then becomes poisoned and no more reaction will take place after a few hours.

Reactions for which tungsten sulfide catalyst has been developed, i.e. the hydrogenation and splitting of oils under high pressures, e.g. 200 atm., proceeds at a technologically satisfactory rate only at higher temperatures. Before discussing this most important field of application, a few examples of partial reactions will be given, which take place either concurrently or consecutively in the catalytic hydrogenation under pressure, and which all may be carried out with the single tungsten sulfide catalyst.

Most results have been obtained in reactions carried out industrially, the rest in experiments with the participants of the reaction kept in motion. The thru-puts in such cases were selected in such a way as to permit the use of the results in technical systems.

A few reactions proceeding without changes of the carbon framework are shown in the table.

REACTIONS ON TUNGSTEN SULFIDE
WITHOUT CHANGES OF THE CARBON FRAMEWORK

Type of Reaction	Example	Conditions of Reaction: Temp. °C.	Pressure Atm.	Partial Pressure of oil Atm.	Thru-put kg/li Cat./Hr.	% Conversion
Hydrogenation of olefins	diisobutylene → isooctane	216	250	20	2.0	99
Hydrogen. of aromatics	$C_6H_6 \rightarrow C_6H_{12}$	322	200	3	0.1	99
" "	naphthalene → decaline	336	200	3	0.9	90
Naphthene dehydrogenation	Methyl cyclohexane → toluene*	485	50	6	0.5	90**
" "	Cyclohexene → benzol	485	50	6.5	0.5	80**
Reduction of organic oxygen, nitrogen and sulfur compounds	Prehydrogenation of brown coal m.o. with 18% phenols,					99.5
	4% nitrogen bases	380	200	8	1.0	99.5
	2.5% sulfur compounds					99

Footnotes to table on preceding page:

* - Tungsten - nickel sulfide catalyst
** - Nearly equal to equilibrium value

We mention here the hydrogenation of hydrocarbons with double bonds. It proceeds successfully a little above 200°, with the olefines being practically completely hydrogenated, as shown on the example of di-isobutylene to iso-octane. Higher temperatures are required to hydrogenate aromatic compounds, somewhat over 300°C, and the hydrogenation of naphthalene to decahydronaphthalene proceeds more readily than that of benzol to cyclohexane.

The tungsten sulfide catalyst naturally accelerates also the reverse reactions, namely, the dehydrogenation. Equilibrium conditions require here higher temperatures. Even at the lower hydrogen pressure of 50 atm., the temperatures have to be much over 400°C. At these temperatures, tungsten sulfide acts as a splitting catalyst and e.g. cyclohexane at 500°C. and 50 atm. hydrogen pressure splits very rapidly. The addition of NiS, or other catalysts like it, largely suppress the splitting action of tungsten sulfide, and cyclohexane or methyl cyclohexane are as largely converted into benzol or toluol without deterioration of the catalyst, as may be expected from equilibrium considerations.

It may be mentioned in this connection that the splitting action of tungsten sulfide is much smaller at ordinary pressures. Cyclohexane and similar naphthenes are dehydrogenated with no splitting. Mineral oils as well can be dehydrogenated at ordinary pressure and temperatures of 400-450° with splitting off of hydrogen and very slight breaking down. Presumably the reaction proceeds in such a way that lower-hydrogen, difficult-to-split compounds are very rapidly formed and splitting is prevented. However, the catalyst will deteriorate as a result of deposition of lower-hydrogen condensation products upon it.

Such carbonaceous deposits upon the catalyst, formed by dehydrogenation and condensation reactions, play an important role not only in the catalytic cracking of oils with no hydrogen; they also are an important cause of the gradual loss of activity of the catalyst during hydrogenation at high pressures. We know how to avoid it by the choice of proper boiling range, purity of the raw materials, sufficiently high partial pressure of hydrogen, and avoidance of too high temperatures. Carbon-containing depositions are not necessarily harmful in all reactions. However, whenever they do disturb reactions and cannot be avoided, it is preferable to avoid the use of tungsten sulfide as a catalyst and use instead one which can be readily regenerated by burning off the carbonaceous depositions upon it.

Another reaction proceeding without changes in the carbon framework is the reduction of organic oxygen and sulfur compounds. We will use here as an example the prehydrogenation of brown coal middle oil instead of a pure compound. The phenols, nitrogenous bases and sulfur compounds in the oil are practically completely reduced to hydrocarbons at about 400°, and it remains to be found to what extent the inhibiting action of these substances or of the products of their reactions at the required relatively high temperature is responsible for the reduction of phenols or the nitrogen bases.

The table below tells about some simple reactions with changes in the carbon framework which proceed in the presence of tungsten sulfide. The required temperatures in this case are about 400°, when there already is some gasification in addition to the principal reaction.

REACTIONS WITH WS_2
INVOLVING CHANGES IN THE CARBON FRAMEWORK

Type of Reaction	Example	Conditions of Reaction: Temp. °C.	Pressure Atm.	Partial Pressure of oil Atm.	Thruput Kg/li Cat./Hr.	% Conversion
Isomerization	n-butane → i-butane	400	200	160	0.5	35
	cyclohexane → methyl cyclopentane	400	250	27	1.0	90
	benzol → methyl cyclopentane	408	250	27	1.0	90
Splitting of paraffins	i-octane → lower boiling hydrocarbons	400	250	18	1.5	40
	min. oil → gasoline 250-320° 180°	400	220	5	1.0	90
	n-heptane → lower boiling hydrocarbons	435	250	20	1.5	15
Splitting of naphthenes	decaline → lower boiling gasoline	408	220	6	1.1	90

Some isomerization reactions proceed without changes in molecular weight. Isobutane, required for the production of isooctane, is produced from n-butane. The 35% conversion shown in the table represents approximately the equilibrium relationships between the n- and i-butanes at the conversion temperature. Another readily proceeding isomerization reaction is the transformation of cyclohexane into methyl cyclopentane. The conversion proceeds with about 90% efficiency, accompanied by a small gasification, again to the production of equilibrium conditions. Under these conditions, benzol is completely converted into cyclohexane and this then is followed by the production of methyl cyclopentane.

Paraffines split at 400°C. and at a pressure of 200-300 atm., e.g., isooctane breaks down into lower-molecular weight hydrocarbons. A mineral oil, b.p. 260-320°C., which consists largely of straight chain hydrocarbons, is readily split into gasoline, b.p. 180°. The splitting of the n-heptane, with a lower molecular weight, requires much more sharply defined conditions, as shown by the low conversion of only 15% at a temperature of 435°C. Isomerization proceeds side by side with splitting.

The splitting of naphthenes, e.g. decahydronaphthaline, proceeds at a high rate at 408°C. More condensed, highly stable ring systems such as perhydropyrene or perhydrocoronene already are partially dehydrogenated. Like the aromatic compounds which they basically are, they are hydrogenated with splitting at lower thruputs and higher pressures.

Observations with pure materials are a valuable aid to the industrial chemist in judging catalysts; however, reactions of a catalyst with practically available raw materials are of deciding importance. The catalytic properties of tungsten sulfide were discovered in technical reactions and they still remain of fundamental importance for the development of the process. The manifold applications of the tungsten sulfide catalyst will be shown on a number of illustrations.

We shall present first a few examples of refining hydrogenation. The hydrogenation of diisobutylene has already been mentioned and is an example of a reaction with a pure product which is also carried out industrially. It usually is run in practice at much lower pressures than 250 atm.

Generally speaking, several simultaneous or consecutive reactions take place industrially, as shown in the table below. The catalyst and operating conditions must be so selected that the desired reaction be chiefly accelerated.

EXAMPLES OF REFINING REACTIONS OF HYDROGENATION WITH TUNGSTEN SULFIDE

Process	Reaction Conditions: Temp. °C.	Press. Atm.	Partial press. of oil	Thruput kg/li/hr.	Principal React.: Hydrogen. of	Reduct. of	Side react. splitt. to lower b.p. products
Refining of crude gasoline to motor fuel	320	40	3	1.25	olefines	S, O	0
Low temperature hydrogen. of brown coal tar to gasoline, lube and paraffine	360	300	liquid phase	0.5	Aromatics olefines	O, N, S	10
Prehydrogenation of liquid phase products from brown & bituminous coal	370	200	8	1.0	aromatics olefines	O, N, S	10

The refining of raw gasoline is done at 300° and involves the hydrogenation of olefines and an almost complete reduction of the sulfur and oxygen compounds. The unwanted hydrogenation of aromatics may be almost completely avoided by the use of not too high pressures so that the refined motor fuel would contain at most 5% hydrogenated aromatics.

Another refining hydrogenation with tungsten sulfide in the liquid phase is the so-called low temperature hydrogenation of tar in low temperature coking of brown coal. In addition to the hydrogenation of olefines and the reduction of oxygen, sulfur and nitrogen compounds, the aromatic rings, as far as they are found in asphalts, are sufficiently hydrogenated to produce in one step anhydrous gasols, good lubricating oils and pure paraffines from the brown coal tar. The diesel oil obtained by distillation of low temperature coking tar from brown coal contains about 14% phenols and has a cetane number of about 20. The low temperature distillation diesel oil is practically free from phenol and has a cetane number of 50. The lubricating oil obtained from the high-boiling gum and asphalt-containing oils is a machine oil with a good temperature-viscosity curve.

The so-called prehydrogenation of middle oil is a similar reaction. It is of great industrial importance, especially with later developments of catalysts made with an eye to sparing the scarce tungsten and the improvement in the quality of the gasoline, since it has been found satisfactory not to convert the liquid phase feed from coal, tar or crude oils in one step into gasoline but to first prehydrogenate them and benzinate them later. The nitrogen, oxygen and sulfur compounds are reduced in the prehydrogenation while the olefines and some of the aromatics are hydrogenated. What prehydrogenation middle oil is not used for the production of gasoline may be used as a good diesel oil. With the conditions more strictly defined, the hydrogenation of middle oil from the aromatic bituminous coal middle oil can be used for the production of oxygen-free kerosene. The gasoline produced in the prehydrogenation, unless derived from the liquid phase, is produced mostly not by splitting of the middle oil, but from the reduction of phenols.

Instead of the tungsten sulfide catalyst, a dilute tungsten sulfide catalyst is frequently used in the prehydrogenation. The present raw material situation forces us to reduce the tungsten consumption to zero. The benzination catalysts are being developed along the same lines.

Before proceeding with the discussion of benzination, we will discuss the technical improvements of lubricating oils. It is accomplished by an intensive hydrogenation of aromatics present in low grade lubricating oils and from such oils lubes are produced with a flat temperature-viscosity curve, while at the same time eliminating the sulfur compounds. The proportion of splitting is greater in this process than in the prehydrogenation because the high molecular weight raw materials have a greater velocity of splitting than the middle oil. About 30% lower boiling hydrocarbons are thus formed. High pressures, say 700 atm., cause the velocity of hydrogenation to become greater than that of splitting. Higher pressures are therefore favorable to that reaction although good results are obtained with tungsten sulfide even at 250 atm. The catalyst plays a deciding role. Thus, working at 1000 atm. without a catalyst does not result in the production of a lubricating oil with a flat temperature-viscosity curve.

The splitting hydrogenation of middle oils, called for short benzination, is the principal step in the production of motor and aviation gasolines and is therefore predominantly important. Its course determines not only the yield but the quality of gasoline as well. Hydrogen under high pressure causes the catalyst to affect not only the rate of hydrogenation but of splitting as well.

Two illustrations of the splitting hydrogenation of middle oil are shown in the table below:

ILLUSTRATIONS OF SPLITTING HYDROGENATION WITH TUNGSTEN SULFIDE

Process	Conditions of Reaction: Temp. °C.	Press. Atm.	Partial press. of oil Atm.	Thru-put kg/li/hr.	Principal reaction splitting to low boiling products	Side Reactions: Hydrogenation	Reduction
Gasoline product. from paraffinic mineral oil m.o. (single pass)	300	300	15	1.0	60	olefines	S
Gasoline Product. from brown or bitumin. coal m.o. (single pass)	400-420	200-300	12	1.0	50	olefines aromatics	O, N, S

High-hydrogen paraffinic middle oils, e.g. from mineral oil, can be relatively readily split at temperatures as low as 380° and give gasolines stable in storage. Benzination of brown and bituminous coal middle oils with tungsten sulfide requires higher temperatures, and phenols and nitrogen compounds may exert a moderating action at the higher temperatures. The gasolines obtained are completely refined, stable in storage and free from unsaturated compounds. With no catalyst, no reaction was found to have taken place under the same operating conditions. In the gasoline production, tungsten sulfide has produced a great increase in the velocity of the reaction and gained through it an importance in the whole process.

Other catalysts, besides tungsten sulfide, find today application in the benzination. The "dilute" tungsten sulfide catalyst has been mentioned and it contains only 5% the amount of tungsten sulfide per unit volume, while the active carrier is an HF treated bleaching earth with its own splitting action. This catalyst possesses a strong splitting and slight hydrogenation activity and produces lower-hydrogen, better anti-knock gasolines, higher in isoparaffinic hydrocarbons. Suitable additions to tungsten sulfide, e.g. of iron sulfide, permit its use under suitable conditions to the production of high-aromatics gasoline from bituminous coal middle oils if such gasolines are produced by dehydrogenation of hydrogenation gasolines. However, these references to mixed catalysts lead us outside the scope of today's discussion.

It was intended to show by means of quotations from our work how universally a single substance, after suitable preparation, may be used as a catalyst in the numerous reactions of hydrogenation of coal. Many things contribute to the development. A close connection between laboratory experiments and industry is essential for rapid progress. We must, however, never fail to use the help obtained from pure science.

It may be just as important for a technical man to learn of scientific developments as for the scientist to hear from a field which has become of importance as a result of the war which has helped bring it to the present stage of development by a combination of inventiveness and systematic research.

In conclusion, the author acknowledges help received from his collaborators in preparing the lecture.

W.M.Sternberg
12-4-1945

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

Stettin-Poelitz
November 10, 1943

OPERATING EXPERIENCE WITH CATALYST 7846-W-250 (8376) AND A COMPARISON WITH 5058 AND A COMBINATION OF THE TWO CATALYSTS

(Translator's Note. This collection of microphotographs was not complete, and some of it illegible. It was considered of sufficient interest to translate the available pages).

Summary of Results:

Operational tests were carried out from April to August 1943 with the three-converter, 7846-W-250 stall, and a comparison of it with the two-converter, 5058 stall and with a stall containing the combination of catalysts: converter I - 5058 catalyst, converters II and III - 7846-W-250 catalyst; and the catalyst combination: converters I and II 7846-W-250 catalyst and converter III 5058 catalyst.

The injection feed was a mixture of 30-40% A + B middle oil from the Roumanian crude oil and 60-70% of a mixture of about 70% of middle oil from coal and 30% middle oil from tar hydrogenation.

The catalyst 7846-W-250 behaves at lower temperatures like the catalyst 5058. The heat of reaction is very great in the first converter. Lowering of temperature 2.0 - 2.5 mv at the inlet to converter I (against about 1.5 mv with the 5058 catalyst) has been found desirable because a uniform distribution of reaction among the three converters was impossible by reason of the great heat of reaction and an undesired rise in the intake temperature in comparison with the behavior of the 5058 catalyst. This procedure with the 7846-W-250 stall offers no difficulties from the operational standpoint because of the activity of this catalyst.

The thruput with the 5058 stall was 0.5-0.7 kg/li/hr. on the average but with comparable conditions the average thruput of the 7846-W-250 was 0.8-1.0 kg/li/hr.

The hydrogenation properties of 7846-W-250 catalyst are sufficiently good in comparison with catalyst 5058.

(Two sentences unreadable).

The gasoline concentration in the catch pot was highest in the 7846-W-250 stall and in the stall with the combination

of catalysts: converter I - 5058 catalyst, converters II & III - 7846-W-250, while the final boiling point was the lowest. This results in a better gasoline production in the 6434 step.

Catalyst 7846-W-250 is distinguished by its extraordinarily good reducing properties for phenols. Most of the phenols (up to 80%) are reduced in converter I, unlike the 5058 catalyst with which the reduction of the phenols is spread uniformly over all the converters. With the 7846-W-250 catalyst, all phenols over the whole boiling point range are reduced equally well, while with the 5058 catalyst the higher boiling phenol fractions are more readily hydrogenated than the lower fractions.

The reduction of nitrogen is sufficiently good with the 7846-W-250 catalyst, which permits a perfect operation of the B middle oil with the 6434 catalyst.

The aromatic content was smaller in the 7846-W-250 stall, while the naphthenes were somewhat higher than in the corresponding gasolines made in the 5058 stall.

No particular differences were found when comparing results obtained with the 7846-W-250 stall with the combination of 5058 catalyst in converter I and 7846-W-250 in converters II and III. The combination stall produced more splitting and hydrogenation, which was to be expected from a comparison of the pure 5058 and 7846-W-250 stalls.

The combination stall: converters I & II, 7846-W-250, and converter III, 5058, was used by increasing the temperature in converter I from 18 to 21 mv while the intake temperature of converter III was 19 mv. With this method of operation, the reaction in converter III was but slight. However, the energy consumption of the stall was rather high. The heat of the reaction was not increased in converter III by raising the intake temperature, but the energy consumption of the stall was greatly reduced.

Most of the phenol reduction was in converter I, as was to be expected. The weak reaction of converter III was, however, sufficient to produce a good phenol reduction and good benzination properties in the middle oils.

(Apparently the balance of the above summary has not been microfilmed.)

<u>Operations of the Pure 7846 Stall in Comparison with Pure 5058 Stall and a Combination Stall (5058 being used first).</u>

It was intended to compare the operations of the pure 7846 catalyst with the pure 5058 and the combination of the two. The observations could be arranged in so many different ways, as to offer but rarely an opportunity to compare all the stalls (pure 5058, pure 7846 and a combination stall with the 5058 used in the first position) under comparable conditions, namely with an equal load, equal combination of injection and equal age of the catalysts. During comparison, the following characteristics were emphasized:

1. Beginning and operating temperature.

2. Reaction behavior with respect to amount of injection and with changes in mixture.

3. Possible load.

4. Hydrogenation and operating properties as well as chemical changes in the corresponding gasolines.

The inlet temperature in the 5058 stall was 17.5 mv., however when starting the pure 7846 it has been found that the catalyst began operating at 15.2 mv. There was a danger of formation of liquid above the catalyst, and for that reason operations of both the 5058 and the 7846 stalls were begun at somewhat higher temperature of 18.0 mv. While doing this, one could notice that the 7846 catalyst required no higher operating temperature, determined by the phenol reduction, than did the 5058. With the 5058 stall, the phenol reduction of the three converters could be made to equal 30% in each converter, which was impossible in the 7846 stall. The hydrogenation action of the pure 7846 catalyst was so intensive already in the first converter that even after ninety days 80% of the total phenols were reduced even with an inlet temperature below 18 mv. Distribution of the work upon the rest of the converters was only possible by a normal rise of the inlet temperature which was undesirable because of the reduced time of contact. This surprising result could only be explained by a higher heat of the reaction in the 7846 converters. The amount of cold gas used was 50% higher with 7846 than with 5058 at the same age of the catalyst and with the same production load. Thus 17,000 m^3 of cold gas in converter I (this was gradually reduced back to 7,000 m^3 in the course of eight months) was by no means uncommon with this catalyst. The regulation of the temperature must for this reason be done with greater care than with 5058. With the latter, the temperature was generally kept within 1.5 mv., but with 7846, 2 - 3.0 mv. difference between converter inlet and outlet is the general rule. A smaller rise during operations would mean wasting the available energy.

This surprising operation of converter I with its high heat of reaction and large amount of cold gas does not represent, however, a danger signal for the safety of the stall, but imposes caution in increasing the reactive composition of the injection (coal or A middle oil) upon which 7846 catalyst reacts. When, however, the characteristic amount of cold gas has been reached, the temperature, unlike with 5058, will drop with the least reduction of the injection. When the injection is reduced by only 1/2 m^3, the temperature drop in converter I can no longer be maintained by reducing the amount of cold gas, and brakes have to be applied by using a greater amount of preheater energy. The same is true when the catalyst is deprived of coal or A middle oil by increasing mineral oil content in the injection by only a few per cent.

The load capacity of 7846 stall is large according to present experience. The load of the 5058 stall was 0.5 - 0.7 kg/li/hr., while 7846 was comparatively successfully used with a thruput of 0.8 - 1.0 kg/li/hr. Perfect heat exchange with a good K value was here assumed. The inlet temperature in converter I was 18.5, the outlet temperature in converter III was 22.0 mv. The proportion of mineral oil in the injection feed acts in general as a limitation upon 7846, not because of the reduced heat of the reaction but by affecting the benzination properties of the catchpot products. Apparently the rule that the a.p. difference becomes smaller with increasing proportion of mineral oil seems to be valid only with respect to the phenol reduction. In an injection feed with 30% mineral oil, with the balance composed of coal and tar in proportion 60:40, a complete phenol reduction was obtained with an a.p. difference of 20°, but good benzination properties were only obtained with a difference of 32°. It seems, therefore, that as the proportion of mineral oil in the injection feed was increased, the nature of the products found in the catchpot depended on the quality of the raw materials used and the benzination was reduced the more, the higher the proportion of the S middle oil from crude oil.

No such difficulties are experienced with 5058. True, a higher temperature may be necessary for the same phenol reduction and this necessarily will result in a greater a.p. difference. However, this difference becomes in most cases equalized, because as a result of better operating properties of 5058, it can be operated with a reduction of 0.05% in the catchpot and the specific gravity becomes lower (cf. the comparative tests on the operating properties in the next section.)

Comparative results on the phenol reduction, specific gravity and changes in a.p. of the individual fractions of the catchpot product of the combination stalls with pure 5058 and 7846 stalls showed that the lower fractions were somewhat more strongly hydrogenated with 7846 and the higher fractions somewhat less hydrogenated, than with 5058. As was to be expected, the combination stalls gave intermediate results (see appendix sheets 1, 4 and 5).

The corresponding changes in specific gravities are shown on sheets 3, 4 and 5.

The phenol reduction (sheet 2), with the 7846 catalyst, is higher behind converter I than with the 5058 catalyst. Moreover, the higher and the lower fractions were equally well reduced, while with the 5058 the lower fractions were only moderately reduced. If 5058 is to be operated to the same phenol reduction, the specific gravity in the catchpot must be lower at a higher temperature, and this results in a greater proportion of gasoline formed.

This is the explanation of the higher total production in the benzination tests on a small scale, invariably obtained with the 5058 catchpot during hydrogenation to the same phenol reduction reaction.

We did not know why the production calculated with the omission of the gasoline introduced with the injection in the 7864 stall was invariably lower than for the 5058 stall. To explain it, the boiling point curves of the catchpot product were plotted in comparable tests at suitable time intervals prior to and subsequent to the removal of gasoline up to 165°. It could here be established that the boiling point curve of the middle oil of a 7846 catchpot was considerably leaner in the bottom part, than that of the middle oil from a 5058 catchpot. The curve of the combination stall occupied an intermediate position.

It would, therefore, be risky to claim that the poor capacity for benzination of the middle oil from the 7846 coil, could be explained by some as yet unknown substances, possibly removable by suitable scrubbing, because the different presplitting of the middle oil, and the boiling point curve connected with it, will give under otherwise equal conditions a very different factor for the benzination properties of the 6434 stall (see presplitting in the 6434 tests).

Corresponding to the different splitting and hydrogenation of the individual fractions, there are found to be different proportions of aromatics and naphthenes in the gasoline, which explains the difference in quality when produced over different catalysts.

The following characteristics data of gasolines from prehydrogenation stalls were compiled from a larger series of tests.

	7846 stall, alone	Comb. stall 5058 in front	5058 stall alone	Comb. stall (stall 6) 5058 in front (not in use)
Aromatics + unsaturated (per cent)	3.5	5.0	8.5	4.0
Naphthenes (per cent)	54.0	50.5	59.5	54.0
Paraffines (per cent)	42.5	44.5	52.0	42.0

The 5058 gasolines had the least amount of naphthenes, while the 7846 had the greatest. On the other hand, 5058 gasolines had the most aromatics and paraffines, and 7846 the least. The combination stall occupied the intermediate position. Stall 6 is a three-converter combination introduced for purposes of comparison, in which the activity of the first converter, filled with 5058, was irreversibly damaged by tailings. This stall behaved as a two-converter 7846 and produced correspondingly gasoline of the same composition.

Taking into consideration, the different hydrogenation and splitting behavior of the different catalysts discussed above, one might draw the conclusion that the 7846 catalyst hydrogenates aromatics more than 5058, but that the naphthenes formed are less strongly split by it. Much caution must be used in drawing this conclusion because of the absence of information on the life of this catalyst at higher temperatures. It is entirely possible that if the 7846 catalyst be operated ata higher temperature it would bring about more splitting because of its higher benzination value as compared with the 5058 catalyst, and the greater hydrogenation capacity of 7846 for the lower fractions would also be carried over to the upper fractions.

(The concluding pages of the report are unreadable).

W. M. Sternberg
1/2/47

Nitrogen Section EB/Op. 462 Oppau, March 9, 1942

METHANE SPLITTING IN THE K PLANT AT HEYDEBRECK

A) Splitting in equipment for gas for distant transmission.

3,500 m^3/h methane per system is to be split.
The temperature in the converter outlet is 850°, methane preheated to 650° C.

Analysis:

	analysis at inlet	CH reaction		water gas reaction	split gas parts	split gas %
CO_2	-			+ 0.225	0.225	7.0
	-	+ 0.487 O_2				
CO	-		0.994	- 0.225	0.769	23.8
H_2			2.008	+ 0.225	2.233	69.0
CH_4	1.000		0.006		0.006	0.2
Dry Gas	1.000				3.233	100.0
m^3 H_2O	1.000	- 0.020	0.980	- 0.225	0.755	
g H_2O	735				556	

K, theor. = 1.16 at 850°

I.) Calculations of CH_4 converter.

a). oxygen required = 0.487 m^3 O_2/m^3 CH_4

b). heat balance of the converter

Heat produced:

Reaction I: $CH_4 + 1/2\ O_2 = CO + 2\ H_2$
Heat of reaction at 650°: 269 h.un/m^3;
0.974 x 269 = 262 h. un.
Reaction II; $CO + H_2O = CO_2 + H_2$
Heat of reaction at 650°: 337 h.un./m^3;
0.225 x 337 = 76 " "
Heat produced 338 " "

Heat consumed:

Reaction III; $CH_4 + H_2O = CO + 3\ H_2$
Heat of reaction at 650°: - 2689 h.un/m^3;
0.02 x 2689 = 54 " "

Heating of split gas from 650° to 850°;
$\Delta T x C_p$ = 200 x 1.322 = 264 " "

True specific heat of the split gas at 800° C

CO_2:	0.225 x 0.563 =	0.127
CH_4:	0.006 x 1.065 =	0.006
H_2O:	0.755 x 0.419 -	0.316
diatomic:	3.002 x 0.330 =	0.992
		1.441 x 0.917 = 1.322

Heat losses 20 h.un.

Heat consumed (heat units/m^3 CH_4) = 338 h.un.

II.) Cooling of the split gas.

a) heat content of the split gas at catalyst converter outlet. sensible heat:

$T \times c_p = 850 \times 1.257 =$ 1068 " "

Average sp. heat of the split gas between 0 and 850° C

CO_2:	0.225 x 0.503 =	0.114
CH_4:	0.006 x 0.746 =	0.005
H_2O:	0.755 x 0.390 =	0.294
diatomic:	3.002 x 0.319 =	0.958
		1.371 x 0.917 = 1.257

Heat of condensation of water: 0.556 x 595 = 331 " "

Heat content at outlet of converter (ht.un./m^3 CH_4) 1399 " "

b) Heat exchanger

The standpipe is disconnected. The split gas, immediately upon leaving the catalyst converter, enters the heat exchanger. The inlet gases are heated to 650° in the heat exchanger.

Heat contents of inlet gas at 650° C:

$650\ c_p + W.L_o = 650 \times 1098 + 0.735 \times 595 = 713 + 437 = 1150$ h.un.

Average spec. heat of inlet gases, between 0° and 650°C

CH_4:	1.000 x 0.661 =	0.661
H_2O:	1.000 x 0.382 =	0.382
O_2 :	0.487 x 0.316 -	0.154
		1.197 x 0.917 = 1.098

The oxygen is practically dry when let in, and at a temp. of 15°. Its heat content is 0.487 x 15 x 0.917 x 0.311 = 2 h.un.

Methane may be heated in the evaporator to 67.5° (v. Section III) and saturated with 206 g. H_2O. Its heat content will be 156 h. un. The heat content is raised from 0.529 x 643.8 = 340 h. un. to 496 h.un. by the addition of 529 g. make-up steam at 1.5 atm. = 111° C.

(After the addition of steam the partial pressure of water is 1/2 P, where P = 956 mm, or by 478 mm (notice: text gives 438 mm). The dew point is at 85.3° (notice: for 438 mm; 87.5° for 478 mm; the rest of the calculations not checked. W.M.S.) The heat content at the dew point is 501 ht. un. (v. III, a1). Upon the addition of steam at 1.5 atm., CH_4 is therefore not entirely dry).

The split gas must therefore give up 1150-(2+486) = 562 ht. un. in the heat exchanger. It leaves the exchanger with a heat content of 1399-652 = 747 ht. un./m^3/CH_4. Its temperature is

$$(747-331) : 1.322 = \frac{416}{1.32} = 315^\circ$$

III. The cooler-vaporizer system.

a). Heat balance of water circuit.

The heat given up to CH_4 in the vaporizer = heat contents of the fresh condensate + the heat taken up in the cooler.

1). Heat given up to CH_4 in the vaporizer.

Heat contents of CH_4 saturated with water = Cp T + WL_T with P = 1.3 atm = 956 mm Hg, $W = \frac{P}{956-P} \times \frac{18}{24.5} =$

$0.735 \times \frac{P}{956-P}$

The average specific heat of CH_4 between 0° and 100° is 0.429 x 0.917 = 0.395.

T, °C	P, mm	W	W x L_T	Cp x T	Heat Cont.
15	12.8	0.010	6	6	12
30	32	0.025	15	12	27
45°	72	0.060	37	18	55
57	130	0.116	72	22	94
60°	149	0.136	84	24	108
67	205	0.201	126	27	153
68	214	0.212	133	27	160
85.3	441	0.628	398	34	432
87.5	478	0.735	466	35	501

The heat transferred to CH_4 in the vaporizer depends on the temperature of the water heated in the cooler. The point of equalization of the split gas is 71.5 (v. III a3). The water is heated in the cooler to 69.5°C. CH_4 leaves therefore the saturator with a saturation of abt 67.5°.

Heat contents of CH_4 at outlet from saturator	156 h.u.
" " " dry CH_4 at 15° at the inlet to saturator	6 " "
CH_4 absorbed in the vaporizer a total of	150 " "

2). Heat contents of the fresh condensate

The fresh condensate is brought in at 15° C. Its amount depends on the amount of water condensed from the split gas in the cooler, or else evaporated into the split gas. However, the heat content of the fresh condensate is small, and the condensate requirements can be obtained from an approximation, in which the heat introduced by the fresh condensate is set in the proper order of magnitude. The second computation of the heat balance gives then the above condensation requirements.

CH_4 takes on in the evaporator (v. a1)	206 g. H_2O
Split gas " " " cooler (v. a3)	312 " "
Fresh condensate requirements	518 " "/m³ CH_4

Heat content of fresh condensate 0.518 x 15 = 8 h.un./m³ CH_4

3). Heat removed from split gas in the cooler.

Heat content of split gas saturated with H_2O = C_pT + $W\,L_T$ at 800 mm Hg pressure. The water content is

$$W = \frac{P}{800-P} \times 3.233 \times \frac{18}{24.5} = 2.38 \times \frac{P}{800-P} \text{ kg/m}^3 \text{ CH}_4$$

The average sp. ht. of the split gas 0-100°C:

CO_2:	0.225 x 0.409 =	0.092	
CH_4:	0.006 x 0.429 =	0.003	
diatomic:	3.002 x 0.308 =	0.925	
		1.020	x 0.917 = 0.936

T	P	W	$W \times L_T$	C_pT	Heat Content
20°	17.5	0.053	33	14	47
56°	124	0.436	271	52	323
57°	130	0.462	287	53	340
60.3	152	0.556	347	56	403
61	156	0.566	360	57	417
67	205	0.820	513	63	576
68°	214	0.868	543	64	607
69	224	0.919	575	65	640
71	244	1.045	654	67	721
72	255	1.112	700	67	767

150-8 = 142 h. un./m³ CH_4 must be removed from the split gas in the cooler. The split gas enters the cooler with a heat content of 747 h. un./m³ CH_4 (v.II). Such an amount of heat corresponds to an equalization point of 71.5°. The water can therefore be heated to about 69.5° by the split gas in the cooler.

The heat content at the outlet of the split gas is still 747-142 = 605 h.un. Its temperature is 68°, it's water content 868 g/m³ CH_4. The split gas then takes on 868-556 = 312 g additional water.

b). Determination of the amount of water in the cooler-vaporizer.

The amount of water in the cooler is not definitely fixed, and may be selected between two values. The least amount of water is fixed at 5.4 Kg/m³ CH_4 by the requirement that the water in the vaporizer be always warmer than the gas to be heated (v. fig. 1). The maximum is given by the requirement that the water be always colder than the split gas, or

$$\frac{142}{71.5-68} = \frac{142}{3.5} = 40.8 \text{ Kg } H_2O/m^3\ CH_4.$$

c). Final cooling.

The split gas leaves the cooler with a heat content of 605 h.un/m³ CH_4. It must be cooled to 20° in the final cooler. 605-47 = 558 h.un. must therefore be removed from it. The cooling water must then become heated from 15° to 50°.

The requirements in cooling water are therefore

$$\frac{558}{35} = 16 \text{ Kg/m}^3\ CH_4.$$

Summary:

Oxygen requirements:	0.487	m³/m³	CH_4
Steam requirements	0.529	Kg/m³	CH_4
Condensate	0.518	" / "	"
Cooling Water	16	" / "	"

B). CH_4 splitting in equipment for long distance gas with additional indirect cooling.

I.) CH_4 converters computed as in A).

II.) Cooling of split gas.

a). Heat contents of split gas at outlet from catalyst converter as in A.

b). Heat exchanger.

The heat exchanger for O_2 remains unchanged.

Methane may be heated in the vaporizer to 85.4° (v.III) and saturated with 628 g. H_2O. Its heat content then is 432 h. un. The heat content will be increased by 0.107 x 643.8 = 69 h.un. to 501 h.un by the addition of 107 g. fresh steam at 1.5 atm - 111°. CH_4 will therefore be exactly at the dew point after the steam was added.

The split gas has therefore given up in the heat exchangers 1150 - (2 + 501) = 647 h. un. It leaves the heat exchanger with a heat content of 1399-647 = 752 h.un./m³ CH_4. Its temperature is about 319°.

III. The Cooler-Vaporizer System.

a). Heat balance of the water circuit.

In the cooler-vaporizer circuit an indirect cooler must be installed, which cools the split gas to within 10° above its dew point, i.e. to 70° C.

The heat balance is then:

The sum of the heat taken away from the split gas in the indirect cooler, the direct cooler and the heat content of the fresh condensate equals the heat given up to CH_4 in the vaporizer.

1). Indirect Cooler

The split gas enters with 752 h. un. from the heat exchanger. The sensible heat of the dry split gas at 70° is 70 x 0.936 = 66 h. un. The heat content of the split gas at the cooler outlet is then 348 + 66 = 414 h. un.

752-414 = 338 h.un. can then be transferred to the water in the cooler.

2). Fresh condensate.

The amount of fresh condensate depends on the amount of water condensed in the direct cooler from the split gas. The amount of heat in the fresh condensate is, however, small, and the condensate requirements may be obtained from an approximate estimate of the heat introduced with the fresh condensate. A second computation will then produce an accurate value of the requirements of the condensate.

CH_4 takes on in the evaporator (Section a 3)	628 g.
The split gas gives up in the cooler (Sec. a4) 556-453 =	103 "
Condensate required.	525 g/m^3 CH_4

The fresh condensate will give up 0.525 x 15 = 8 h. un. to the circuit.

3. Vaporizer

The heat transferred to CH_4 in the vaporizer depends essentially on the temperature of the water heated in the direct cooler. The split gas enters the direct cooler with 414 h. un. The dew point with this heat content is 60.9°. The water may then be heated in this cooler to about 57°. The heat content of CH_4 at 57° is 94 h. un. The 338 h. un. of CH_4 transferred in the indirect cooler correspond to a dew point of 85.4°, and to a water content of 628 g/m^3 CH_4.

4. Direct cooler

The amount of heat removed from the split gas in the direct cooler must be sufficient to produce 94 heat un. in CH_4 saturated at 57° from the heat content of dry CH_4 at 15° and the heat content of the fresh condensate. The split gas, when leaving the cooler, still has 414-80 = 334 h. un. The dew point corresponding to this heat content is 56.7° with a water content of 453 g. The amount of water given up in the cooler by split gas is therefore 556-453 = 103 g.

C). Determination of the amount of water in cooler-vaporizer circuit.

The amount of water in the circuit is not definitely fixed, but can be selected at will between two values. The maximum and the minimum amounts are found from the requirements, that the cooling water still possess a finite amount of ΔT at the hot end of the direct cooler with respect to the equalization point of the split gas, and that the water in the evaporator be always warmer than the saturated CH_4. The maximum and minimum amounts are shown in fig. 2, as obtained when the cooling water at the end of the direct cooler, is 2° cooler than the entering split gas. The maximum and the minimum amounts are so small, that some of the water vaporizes at the hot end of the cooler in the form of steam.

c). Final cooler.

The split gas leaves the circuit cooler with 334 h. un.

It must be cooled to 20° in the final cooler.

$334 - 47 = 287$ h. un./m^3 CH_4 are therefore to be removed from it. The cooling water must be heated from 15° to 50°.

The required amount of cooling water is therefore

$$\frac{334}{35} = 9.6 \text{ kg/m}^3 \; CH_4$$

Summary:

Oxygen requirements	0.487 m^3/m^3 CH_4
Steam requirements	0.107 kg/m^3 CH_4
Condensate requirements	0.525 " " "
Cooling water "	9.6 " " "

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W.M. Sternberg
12/13/46

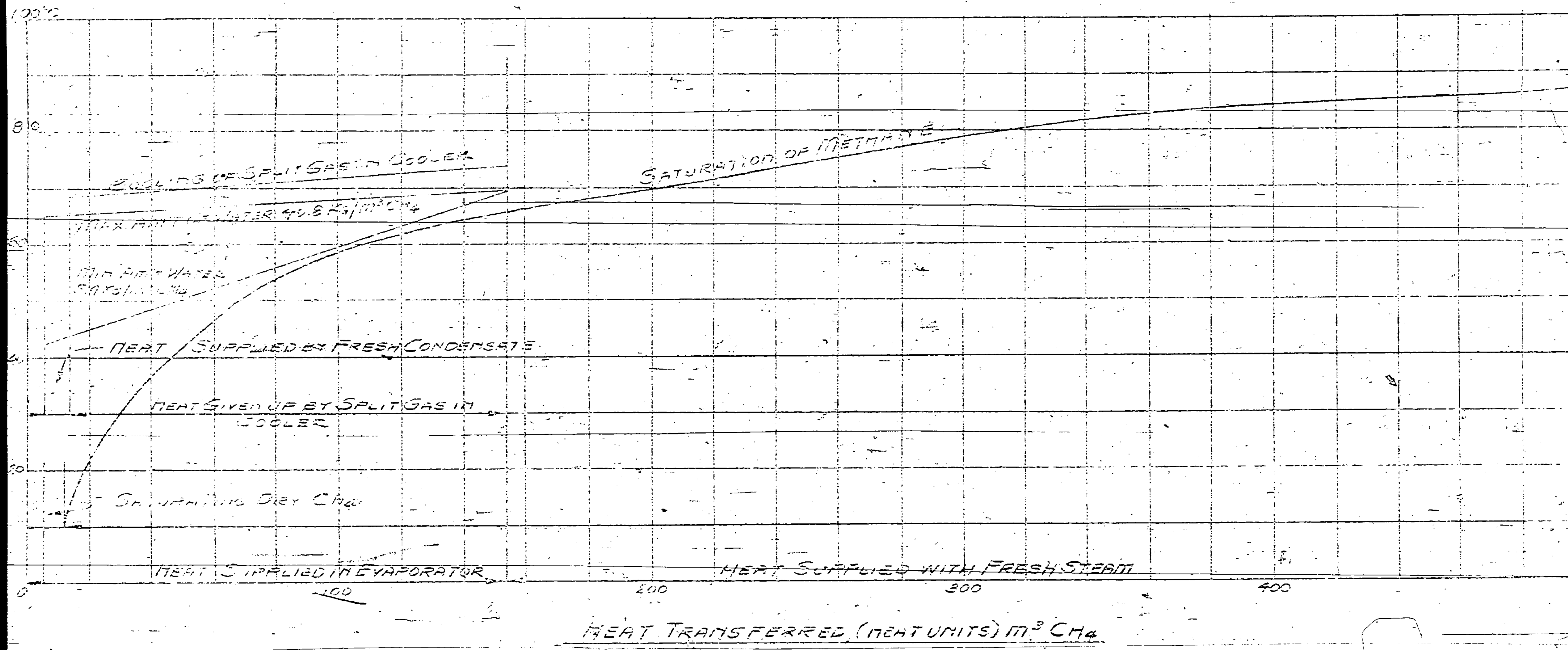
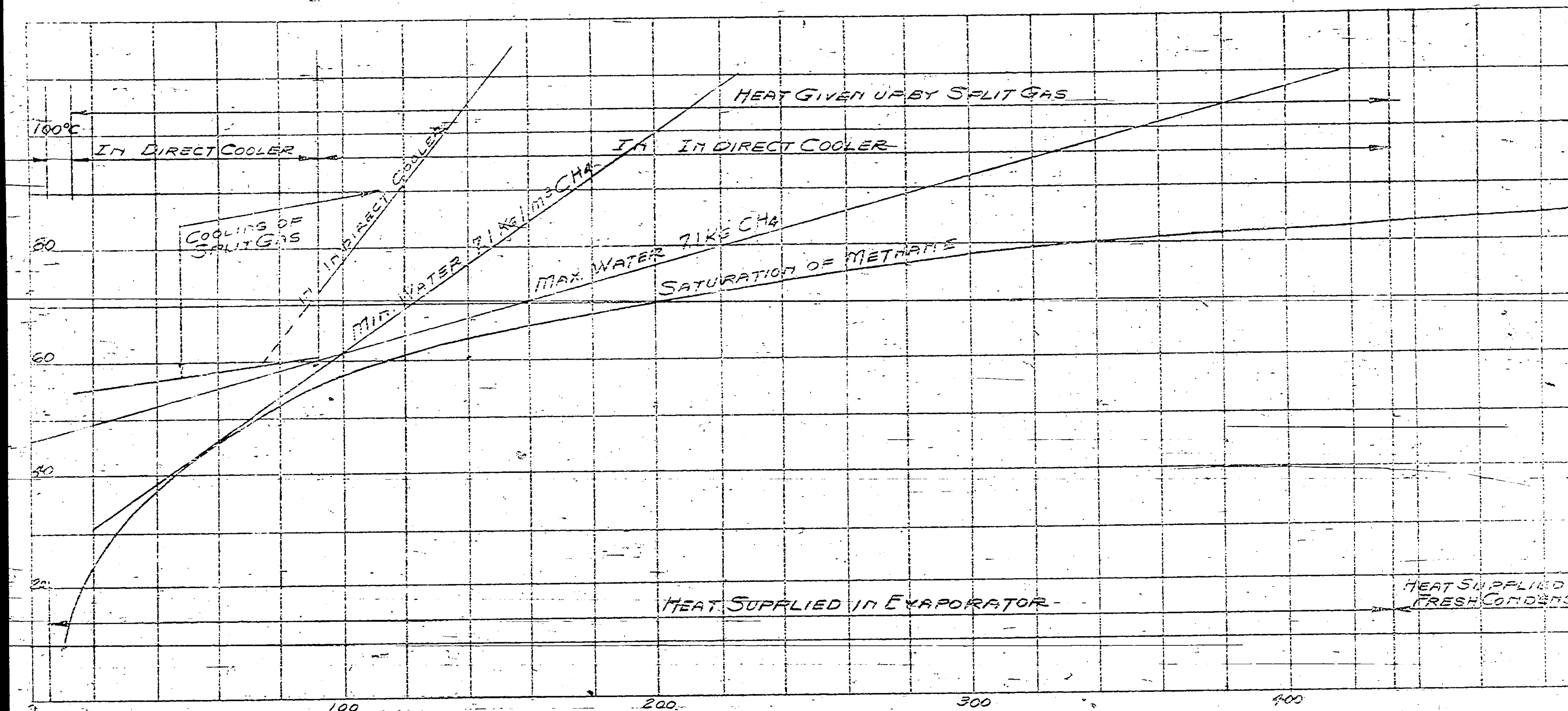
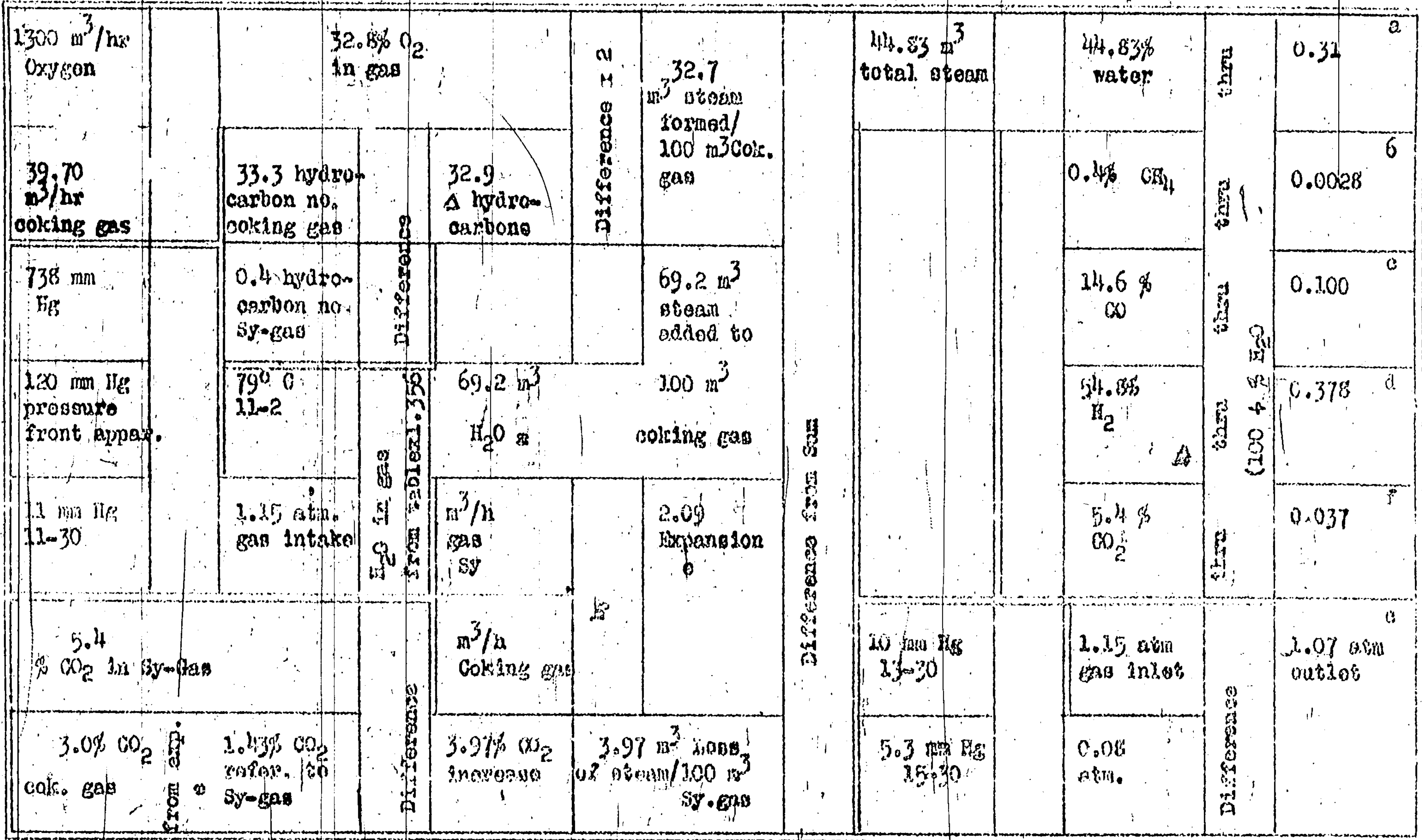

100°C
80
Saturation of Methane
Boiling of Split Gas in Cooler
Max. Amt of Water 40.8 Kg/m³ CH4
Min. Amt Water
Heat Supplied by Fresh Condensate
Heat Given up by Split Gas in Cooler
Saturating Dry CH4
Heat Supplied in Evaporator
Heat Supplied with Fresh Steam
0
100
200
300
400
Heat Transferred (heat units) m³ CH4

Fig. 1



HEAT TRANSFERRED (HEAT UNITS) m^3 CH_4

FIG. 2



K_p = 0.31 x 0.0028 = 0.14

0.1 x 0.0543 x 1.15 2   0.146-1

(methane   0.378   1.07

c   d   e

K_p = 0.31 x 0.1 = 2.21

Watergas   0.378 x 0.037

d   f

Temp.= 1124° C.

T-186, Figure 3.

TOM Reel 129
Ref. a-3
pp. 57-68

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-187

Leuna, Sept. 24, 1943

Accounting in Hydrogenation (abridged translation)

The production costs of hydrogenation products are determined quarterly as the "mixed costs" in the so-called "production accounting" ("Massenkalkulation"). Until recently, the costs were split between motor gasoline, aviation gasoline and diesel oil using set maximum and minimum costs, determined over long periods of time when establishing the guarantee price for the motor gasoline. The costs of the liquefied hydrocarbons ethane, propane and butane were determined separately. In addition to the "production accounting" a "calculated accounting" ("durchgerechnete kalkulation") was used regularly, and here the production costs of the different intermediates were calculated from the production. Special voluminous calculations had to be made for the evaluation of the circulating feeds, which are characteristic for hydrogenation because a simple estimation of these circulating products would have falsified too much the whole accounting picture. The actual value of this "calculated accounting" remained, however, rather slight; it resulted in neither a break-down of the costs of the finished goods depending on their origin (e.g. gasoline from coal and gasoline from tar), nor a break-down of the costs into gasoline and diesel oil. The "calculated accounting" is therefore no longer used since the beginning of the current year. This omission, as well as the omission of the bulky logs of operation, resulted in an important saving in labor. The Government Controller's office, which sets the directives in accounting, has given its approval to this change.

There still remains, however, as before the need to split up the mixed costs according to the nature and origin of the finished goods. This is made necessary for cost supervision and comparison. The supervision of costs is important even in times of war; low costs mean low labor requirements and lowered consumption of raw materials and power. To permit a desired break-down of costs, a form of accounting has been developed which permits a rapid determination of the production costs of the finished products from different raw and intermediate products. It is briefly described below.

Statements of yields are systematically presented by the operational control to permit the finding of the hydrogen consumption and the load upon the different units in the production of aviation gasoline from the different raw materials and intermediates. The cost of hydrogen and the credit for the circulating gas are known and the operating costs can be obtained at the different accounting stations and recalculated per ton input by dividing them by the total input. In this way, costs can be readily calculated from the data on volume furnished by the operation control division for each raw product and intermediate used in the production of aviation gasoline, when the costs of the auxiliary substances are treated in the same way as the costs of operation, e.g., we arrive at the cost of production of one ton aviation gasoline in the second quarter of 1943 (later called the "conversion costs") to be 54.09 RM/te.

Conversion Costs of 1 Ton of Aviation Gasoline From A-Middle Oil

	Input or Consumption/1000 A middle oil	Costs, Rm/ton input, or price/unit	Costs per ton A-middle oil
Materials			
Conv. stall, liq. phase	13.329	1.6000	0.021
" " vap. phase	2,360.538	0.7080	1.672
Scrubbing	797.454	0.0689	0.055
Liquefiable gases	112.956	1.4770	0.167
Total			1.915
Conversion Costs			
Tar centrifuging	13.560	10.7696	0.146
Liquid phase distillation	21.493	2.1422	0.046
Conv. stall, liquid phase	13.329	4.1449	0.055
Scrubbing, rich gas	0.151	49.9050	0.008
Conv. stall, liquid phase	2,360.538	6.8038	16.061
Scrubbing	2,265.987	2.9020	6.574
Stabilization	797.454	0.7856	0.626
Liquefiable gases	112.956	59.6693	6.740
Gasoline testing	859.642	0.0951	0.082
Total			32.064
Make up gas, m^3	752.597	42.6129	31.218
Hy gas, 10^3 heat.un.(credit)	1,496.851	7.4200	11.107
Conversion costs of the vapor phase			54.090
Value of input	1,000.000	124.448	124.448
Prod. costs for gasoline	859.642*	207.689	178.538

* yield/1000

The production costs can be readily found from the conversion costs and the cost of raw materials: e.g.

Aviation gasoline from coal

	t raw brown coal/t aviat. gasoline	Per ton raw brown coal	Per ton aviat. gasoline
Raw brown coal	5.9694	3.095	18.48
Conversion costs	5.9694	31.697	189.21
Production costs	5.9694	34.792	207.69

Aviation gasoline from tar

	t tar/t aviat. gasoline	Per ton tar	Per t aviat. gasoline
Tar	1.2788	98.388	125.82
Conversion costs	1.2788	66.219	84.68
Production costs	1.2788	164.607	210.30

The production costs of the intermediates can be calculated in the same way by subtracting the conversion costs from the production costs, as has been done above in the appendix in the conversion costs of A-middle oil to aviation gasoline. Production costs for diesel oil are equally simply obtained bearing in mind that diesel oil is simply B-middle oil and that in the second quarter of 1943 B-middle oil, worth RM 37.63/t was converted into aviation gasoline with a yield of 903.038/1000.

	to	RM/t aviat. gasoline coal	RM/t aviat. gasoline tar	RM/t coal	Diesel oil tar
Product. costs, av. gasoline	0.903038	207.69	210.50	187.55	190.09
Conv. costs, B-middle oil to av. gasoline (to be subtracted)				37.63	37.63
Conv. costs of diesel oil II				149.92	152.46

It is characteristic for this method of cost accounting that the conversion costs per ton of product are calculated directly from specific amounts, using prices for raw materials, hydrogen, circulating gas and the operation costs per t of the product. In the production accounting, mentioned in the beginning, the mixed costs per ton of the finished products are obtained by dividing the total consumption by the total production, which puts a burden of the total consumption upon the carrier of costs. In the accounting described here, it must first be obtained by a control computation by proving that the sum of the different finished products, multiplied by the corresponding production costs, are actually in agreement with the total expenditure.

It is found convenient in actual accounting to use suitable form sheets, as shown in the appendix (not reproduced here).

/S/ Pichler

W. M. Sternberg
1-6-47

TOM Reel 65
Frames 119-127

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-188

METHOD OF PRODUCTION OF AMMONIA SYNTHESIS GAS

O.Z. 14396
Ludwigshafen/Rh, Sept. 10, 1943
J/K

It is well known, that in the catalytic synthesis of complicated hydro-carbons from carbon monoxide and hydrogen at normal or slightly increased pressure by the Fischer-Tropsch process, or carried out at higher pressures in some other proposals, the synthesis gas is incompletely transformed, in particular when it is progressively more strongly diluted by inert gases in ever increasing concentration, as well as by the newly formed gas and vapor compounds, such as methane, steam, and occasionally also carbon dioxide. The residual gas after the conclusion of the synthesis, upon the separation of the liquid constituents, contains, in addition to the unreacted carbon monoxide and hydrogen, also considerable amounts of methane, carbon dioxide and nitrogen from the original synthesis gas.

This residual gas has until recently been used as a fuel. It is, however, very pure - it contains no sulfur nor other catalyst poisons - and burning it must be considered uneconomical. It has already been proposed to obtain a better use from it by using it as a raw material for the production of synthesis gas by decomposing the methane present in it with steam according to the equation $CH_4 + H_2O = CO + 3 H_2$. This conversion has been brought about either by a return to the producers, or else in special splitting units. However, methane is not in this way completely converted and a considerable proportion of it remains in the gas. Moreover, the remaining nitrogen is undesirable, because it becomes gradually more and more enriched in the gas through the return of the return gas to synthesis, and this will result in a reduction of the concentration of carbon monoxide and hydrogen; this will affect the conversion of the synthesis gas and the utilization of the catalyst space. For this reason, only some definite proportion of the residual gas may be returned and re-split. If, however, the nitrogen in the residual gas were to be removed, this would involve a very expensive decomposition of the gas. This was the reason for using the residual gas as a fuel.

It has now been found that the residual gas from the catalytic reduction of carbon monoxide to complex hydrocarbons, possibly even in the presence of oxygen compounds, can be conveniently used for the production of gas for the synthesis of ammonia. For this purpose it is split by the already familiar methods in the presence of water and/or of oxygen or of oxygen-containing gases, preferably in the presence of catalysts and at high temperatures, and the carbon monoxide present converted in the familiar way with steam.

Hydrogen-containing gases have already been prepared for many purposes by the splitting of hydrocarbons, i.e. for hydrogenation of carbonaceous matter. It was however, unimportant in such cases, if noticeable amounts of hydrocarbons still remained in the gas, because they can be so completely removed from the gas circuit, as a result of their solubility in the liquid hydrocarbons or the other reaction products, that no excessive enrichment of them will take place. On the other hand, methane can not be removed in this way in the synthesis of ammonia, because the solubility of methane in liquid ammonia is much too small for that. Surprisingly, however, the concentration of methane can to such a degree be reduced by splitting, that it will not longer affect the synthesis of ammonia, and no disturbing enrichment will take place, as might have been anticipated.

On the other hand, there exist several advantages in using the residual gas from the reduction of carbon monoxide as a raw material for the ammonia synthesis gas preparation. Not even a larger excess of nitrogen is harmful in the ammonia synthesis, because the presence of nitrogen is even required. The splitting can be carried out at relatively low temperatures, due to the absence of sulfur, and the splitting catalysts as well as the metal splitting unit (in particular iron) will have a longer life. Moreover, the splitting of gas for the reduction of hydrocarbons must be performed in the presence of carbon monoxide and hydrogen in the proper proportion; this is not necessary for the ammonia synthesis. Any carbon monoxide still remaining in the gas is converted to hydrogen. It is practically of no importance what the proportion of cabbon monoxide to hydrogen is present after the splitting of hydrocarbons. Finally, it is often advantageous to have considerable amounts of carbon dioxide during the splitting for the production of ammonia synthesis gas, in most cases between 20 and 65% all or part of which is made use of in the splitting for the ammonia synthesis. Carbon dioxide also reacts with methane, according to the quation $CO_2 + CH_4 = 2CO + 2H_2$. Other gaseous hydrocarbons, such as propane and butane, are decomposed similarly.

It has also been found particularly advantageous when splitting the residual gases with steam to eliminate the still remaining hydrocarbons in the gas by a later oxidation treatment with a mixture of oxygen and nitrogen, in particular air. The required proportion of nitrogen to hydrogen in the ammonia synthesis gas is approximately equal to their combining proportion, and it is therefore generally required to add some nitrogen to the gas. Should this happen in the form of a mixture of nitrogen and oxygen, in particular air, one may succeed in arriving at a complete oxidation of the hydrocarbons. Should a greater proportion of nitrogen be required, the preceding splitting may advantageously be carried out incompletely at high flow velocities and the subsequent oxidation of the hydrocarbons may then take place to a greater extent.

There exists the additional advantage of being able to change readily the amounts of gases for the ammonia synthesis to meet the requirements. This may be done by having greater or smaller amounts of carbon dioxide present during the splitting. We may also vary the amounts of hydrocarbon present during the splitting. Thus, if hydrocarbons with 3, 4 and 5 carbon atoms can be used elsewhere, say for the fuel production, and methane and ethane will split primarily. When however the need for synthesis gas is increased, then the C_3, C_4 and possibly C_5 hydrocarbons, still present after the separation of gasoline, are all or in part used for splitting, when, by way of example, one mol of propane can produce 10 moles of a gas for the ammonia synthesis, according to the equation

$$C_3H_8 + 3\ H_2O = 3\ CO + 7\ H_2.$$

The splitting is best performed in the presence of catalysts. The nickel-magnesia catalysts are particularly well suited for the purpose, when deposited upon a carrier, such as kaolin, alumina cement, etc. (i.e. as in the German patent 552,446). The catalysts may be shaped in a suitable way, i.e. to produce the least resistance to the flow of gas. Hollow bodies are particularly convenient, for instance in the form of Raschig rings. The splitting temperature is usually between 750 and 1000° C. An installation similar to the so-called "tubular process" may be used to advantage (as described in the German patent 570,026).

Steam or air are intimately mixed in the familiar way with the gas to be split.

Should too much carbon dioxide be present in the gas, the undesired excess may be removed in the familiar way, especially by pressure scrubbing, e.g. under pressures of 10 to 50 atm, or else by washing with liquids which break down upon heating or under reduced pressure and thus become regenerated, e.g. water solutions of soda, potash, potassium phosphate, or of organic bases like ethanol amine, diaminopropanol, etc. Solutions of salts of strong bases with weak organic acids, particularly aminoacids, such as sodium alanin (so-called alkacid solution) are especially desirable.

The oxidation splitting which is frequently conveniently made to follow the original splitting, may also be performed in the familiar way; one may well operate here at the same temperature as during the first splitting. Activated nickel catalysts may here be used as well. The hot gas from the splitting converter may be mixed with a sufficient amount of air for the oxidation splitting in a burner, in which a sufficient mixing will take place, and the partly converted gases are lead into the catalyst chamber. The conversion may also be carried out in several steps.

Should the splitting of the residual gases of the carbon monoxide reduction be carried out with a mixture of air and oxygen, with the conversion of most of the carbon monoxide to carbon dioxide, one may operate according to the German patent 558,430. The reaction with oxygen, as well as with steam, may be carried out under pressure, especially if the reduction of carbon monoxide is done under pressure.

After the reaction with steam or with oxygen-containing gases, or with both, the gas is converted, with most of the carbon monoxide changed into carbon dioxide. The steam produced during the splitting (usually 200 to 300 g per m^3 of the final gas) also enters the reaction. It is of advantage during conversion, that the gases are completely free from sulfur. Lower conversion temperatures and less steam will be required. It also acts as a protection of the catalyst. Conversion, splitting and any possible subsequent oxidation may be carried out at ordinary, reduced or raised pressures. The split gas at 900° C is cooled to the temperature required for the conversion of the carbon monoxide by passing it through a waste steam generator, or by spraying water into it, when the steam content of the gas needs be raised.

Gas produced in this way (and freed from carbon dioxide) can be used for ammonia synthesis either alone or mixed with other nitrogen-hydrogen mixtures.

The ammonia synthesis can be performed by any familiar methods.

Example 1.

A synthesis gas obtained by the gasification of solid fuel, and containing 28.5% CO, 55.3% H_2, 0.5% CH_4, 12.5% CO_2 and 3.2% N_2 is freed from organic or inorganical combined sulfur and made to react in two stages at ordinary pressure and 185 to 190° in a plate converter with a catalyst containing cobalt, MgO and kieselguhr, with a deposition of the liquid and solid hydrocarbons formed in each stage. After the separation after the second stage, the gas is led through an activated carbon unit for the removal of the C_3 and C_4 hydrocarbons as well as of any still remaining gasoline hydrocarbons. The activated carbon unit is regenerated with water at regular intervals.

The residual gas contains 52.2% CO_2, 7.9% CO, 11.5% H_2, 14.6% CH_4, 0.7% C_2 hydrocarbons, 1.0% C_3 hydrocarbons and 12% N_2. The C_2 and C_3 hydrocarbons are in part olefines.

About 12,000 m^3 per hour of this gas and 3.9 te steam from a waste heat boiler are passed through a converter with 66 tubes of heat resistant steel, about 6 meters long and 0.15 m in diameter, filled with activated nickel catalyst and heated from the outside to 750° with gas. The hot split gas is mixed in a burner with 2000 m^3 of air and passed for a second time through a layer of the same nickel catalyst. 15,200 m^3 of a gaseous mixture is obtained which contains nitrogen in proportion to hydrogen + CO of 1 : 3, and from which hydrocarbons are removed down to 0.2% CH_4. 5.2 m^3 hot water are sprayed hourly into the gas at 850° to lower the temperature to 400° and to raise the steam content. 18,400 m^3

of gas, composed of 39.2% CO_2, 3.6% CO, 42.0% H_2, 0.1% CH_4 and 15.1% N_2 will be obtained after the conversion of the carbon monoxide over iron catalyst with the steam present in the gas. The carbon dioxide is removed by washing with water under about 15 atm pressure and the rest of the carbon monoxide removed with copper solution after some additional compression. The gas is now used for the synthesis of ammonia. The carbon monoxide removed with the copper solution is added to the carbon monoxide-hydrogen mixture for the production of hydrocarbons.

Example 2.

Synthesis gas, prepared and purified in the same way as in Example 1, but now contains about equal amounts of carbon monoxide and hydrogen (41.0% CO, 42.8% H_2), is led under a pressure of 200 atm at about 183° over an iron melt catalyst in a tubular furnace of good heat conductivity, with the 12 mm i.d. tubes in water boiling under pressure. The gas is passed through in two stages, with the products formed separated after each stage. At the conclusion, the last traces of liquid hydrocarbons are removed in an oil scrubber. The residual gas contains 4.75% CO, 6.4% H_2, 19% saturated hydrocarbons (average C number = 1.2), 2.3% olefines, 56% CO2 and 11.6% N_2.

Carbon dioxide is for the most part washed out under the pressre of the hydrocarbon synthesis with a 30% water soltuion of sodium alanin in a tower with Raschig rings. The used solution is regenerated with steam in a gasifier, cooled to 50° and reused for washing. The washed gas then contains 12% CO_2.

4600 m^3 of this gas are split in an hour with 5.8 te steam in a splitting converter described in example 1, and the split gas containing 3 - 4% CH_4 is further converted upon the addition of 2500 m^3 of air. About 14,000 m^3 of a gas mixture is obtained containing 8.1% CO_2, 17% CO, 53.5% H_2, 0.1% CH_4 and 21.5% N_2. 2.8 to 3 te of steam are required for the subsequent conversion of CO, and it can be added by injecting water into the hot gas. It is however better to cool the gas in a waste heat boiler from 900 to 400° and add the required steam in the form of low pressure steam. The subsequent treatment is as in example 1.

Example 3.

The residual gas treated as in example 2 and partially freed from CO_2, and containing 12% CO_2 , 9.6% CO, 12.8% H_2, 32% CH_4, 4% ethane, 2% propane, 3% ethylene, 1.6% propylene and 23% N_2 is saturated with steam, preheated to 350° in the heat exchanger with the off-gas from the carbon monoxide converter, and combined in a burner with the equally preheated mixture of air and oxygen.

The hot combustion gases at 1100–1200° are first led over a layer of a catalyst composed of nickel upon fire-clay, and next over a layer of an activated nickel catalyst, e.g. of nickel and magnesium oxide. The gases are cooled over the catalyst and leave the converter at about 750 - 800°. A converter holding about 7 m^3 of the two catalysts can convert about 5000 m^3 of the above gas mixture per hour upon the addition of 1400 m^3 of oxygen, 1800 m^3 of air and 1.15 te of steam. About 11,600 m^3 of gas is produced an hour, and it is composed of 9.5% CO_2, 24.2% CO, 43.6% H_2 0.2% CH_4 and 22.5% N_2. The steam content is increased by steam injection and the gas cooled to 400°, CO is then converted with steam and the gas treated as described in example 1.

Patent Claims.

1. Process for the production of ammonia synthesis gas by splitting of short chain hydrocarbons with steam and/or with oxygen or oxygen-containing gases, and occasionally with carbon dioxide, and the transformation of the then present carbon monoxide with steam, characterized by the use as a raw material of a gas obtained as a residual gas in the catalytic reduction of carbon monoxide to lower hydrocarbons, occasionally with oxygen-containing compounds.

2. A process in accordance with claim 1, characterized by following up the splitting with steam with a second splitting with nitrogen-oxygen mixtures, in particular with air.

I.G. Farbenindustrie Aktiengesellschaft

W.M. Sternberg
12/12/46

T.O.M. Reel 181
Pgs. 711-716

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-189

KCBraun
12/10/46

OBSERVATIONS ON CATALYSTS FOR CRACKING AND HYDRO-CARBON CONVERSION

Lu, Nov. 22, 1940

X-Ray Examinations

Synthetic magnesium silicates have a montarillonite structure, like terrana.

Synthetic aluminum silicates are amorphous under x-rays.

Magnesium silicate catalysts of various manufacture show various sizes of crystallites; the finest crystallites are the most active.

Heavy Metal in Cracking Catalysts

Heavy metal in splitting catalysts produces much gas under cracking conditions, which, as a rule, consists of about 80% H_2. At the same time the splitting deteriorates.

Zinc

Zinc (abt. 10%) on Mg-silicate catalyst already produces considerable gas (90% H_2) at 400-430°C. However, the product is little dehydrogenated; rather, a corresponding part of the oil is coked. Small zinc additions tend to retard the splitting to low-boiling (C_3C_4).

Iron

Terrana produces less splitting than super-filterol, but more gas: iron content.

Alkali Addition to Cracking Catalysts

When alkali (K) is added, the split product contains less low-boiling constituents.

Isomerizing in Cracking

Cracked gasoline from Elwerather oil over Mg-silicate has a motor method octane number of 72-74 @ 25% aromatics and little unsaturated (1% according to H_2SO_4 method, abt. 10% according to iodine number). This causes isomerization.

Nitrogen Sensitivity

Mg-silicate is resistant against 0.1% aniline.

Non-Silicate Catalysts in Cracking

Activated alumina splits considerably less than silicates, but is important for splitting of paraffin to unsaturated middle oils.

Activated carbon splits about as super-filterol, but yields less low-boiling (C_3C_4).

It yields a greater gas volume and in this respect resembles terrana and catalysts containing heavy metals.

Synthetic Carriers for Aromatization

Silicates: While silicates (Al or Mg) precipitated with ammonia are inactive, precipitation with lime or, better still, with Mg-carbonate yielded active silicates, which were improved by the addition of Fe and Mn.

Activated Alumina: yields catalysts which are superior in the processing of products containing cresol, and probably also nitrogen, because the silicate catalysts polymerize compounds containing oxygen and nitrogen too rapidly.

Combined Results of the Study of Catalysts for the Conversion of Hydro-Carbons

The studies of catalysts in various fields, such as splitting, dehydrogenation, isomerization, cyclization and polymerization, may be summarized about as follows:

a). Splitting

The most active basic catalysts (mono-substance catalysts) are silicic acid and carbon. Both indicate almost a pure splitting reaction (without additions), as e.g. the decomposition of a paraffin molecule of average chain length into paraffin + olefin of shorter chain. With these catalysts, the splitting takes place about the middle of the chain and, with the use of a gas oil fraction (mol - wt. = 200), yields gasoline (mol - wt. = 100), which is half paraffinic and half olefinic (iodine number = 100). There is very little gasification here. The new formation of aromatics could not be determined.

By activating SiO_2, or carbon with Al or Mg, the splitting capacity is increased considerably, i.e. with the same conversion either the thruput may be increased, shortening the contact time and yielding the same reaction products as before (paraffin + olefin from paraffin), or the conversion may be increased with the same thruput, yielding other products of reaction. Instead of about equal quantities of paraffin + olefin a parafinnic gasoline (iodine number = 30-60) is produced in this case, because the SiO_2 catalysts activated with Al or Mg not only split the paraffin but also polymerize the olefin. Both reactions take place successively, splitting as primary and polymerization secondary. Gasification is higher here than in a pure splitting reaction.

In Al or Mg activated SiO_2 catalysts the increased splitting is combined with an isomerization of the split products, which preferably occurs in the shorter split fragments (C_4 and gasoline components to about 150° C). The butane formed in splitting is 80-90% by vol. iso-butane. Isomerization disappears almost entirely above 150° C and the split B-middle oil shows no further indication of a new formation of isomers (good diesel oil).

Natural Fuller's Earth (Bleicherde) (Al or Mg-silicate), activated with acid, behaves like SiO_2-Al or SiO_2-Mg, but is much weaker.

If the Al or Mg in the SiO_2-catalysts is replaced by Fe, gaseous split fragments appear in large volume facilitating the separation of the C atoms formed.

Al_2O_3 is much less active as a splitting catalyst than SiO_2 or C. Al_2O_3 entirely free of alkali will split better than one containing alkali, but the split fragments are gaseous. No appreciable isomerization is noticeable in the split products obtained over Al_2O_3.

b). <u>Dehydrogenation</u>

When operating with a deteriorating catalyst, Al_2O_3 has proved to be the best component in combination with Mo.

The preparation of an especially active form of Al_2O_3 is dependent upon certain conditions, which are being investigated at the present time in cooperation with Dr. V. Füner. Besides precipitation and washing, heating presumably plays an important part.

Al_2O_3 entirely free of alkali will produce high splitting to gaseous products with relatively little formation of aromatics.

Al_2O_3 catalysts formed in an extrusion press show a distinct reduction in activity compared to individual pieces. (Presumably because of their lower contact surface; longer compared to shorter pieces-?).

Partial replacement of Al_2O_3 by Fe_2O_3 will produce distinctly inferior dehydrogenation catalysts. The same is true of catalyst containing MgO instead of Al_2O_3. Both catalysts produce gasoline of high iodine number.

When dehydrogenating with a deteriorating catalyst, heavy gasoline is split, dehydrogenated and cyclizated. Isomerization probably takes place at the same time, even though to a lesser degree. Furthermore, low anti-knock, paraffinic, heavy gasoline components are removed by gasification and olefinic, split gasoline components are saturated at the end of the catalyst layer by weak hydrogenation.

In testing various charges of alumina it was found that strong displacements may occur within the given reactions. When using variously prepared alumina for the 7360 dehydrogenation catalyst, dehydrogenation gasolines were produced from the same feed gasoline, which differed very much from each other, not only in aromatic content, but also in the iodine number. If suitable alumina are used, it should be possible to produce high performance fuels with an iodine number < 4 without further refining.

Pure dehydrogenation of naphthenes to aromatics is least affected by the quality of the alumina. This reaction is comparatively simple. On the contrary, cyclization is very much dependent upon modification of the alumina. This has been shown in experiments with n-heptane, which may be converted into toluene by catalytic cyclization.

c). Cyclization

After many experiments, together with Dr. V. Füner, a combination of Al_2O_3 and Cr has been found to be by far the most active catalyst. These experiments clearly showed that the alumina best suited for n-heptane cyclization are also the best components of dehydrogenation catalysts. They also showed that various modifications of alumina may be vastly different in their cyclization properties.

d). Polymerization

The polymerization properties of SiO_2-Al_2O_3-catalysts have already been mentioned under the heading of "Splitting", which properties may markedly influence the nature of the split products in catalytic cracking. SiO_2-Al_2O_3 may also be used for the polymerization of gaseous olefins into polymer gasoline, instead of the normally used catalysts based on H_3SO_4 or Cupyrophosphate. Compared to the latter catalysts, the polymerization takes place without pressure, although the position of the polymerides in the boiling curve differs from those obtained over P-catalysts; they contain more components in the middle-oil range.

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U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-190

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12/18/46

Lu, 16 October 1942

DEVELOPMENT OF VAPOR PHASE HYDROGENATION AND OF CATALYSTS IMMUNE TO POISON. (ABSTRACT).

The development of catalysts immune to poison and the development of vapor phase hydrogenation are so closely connected that they must be considered together.

Experiments for the production of amines and the reduction of phenols started in October 1924 in Lu 35, induced the development of poison-proof hydrogenation catalysts.

The black oxide catalyst used for the ammonia synthesis, which thereby lost some of its activity, fully retained it when treated with H_2S. Other sulfides, as those of Co and Mo behaved similarly and showed even greater activity than black oxide. The field of poison-proof catalysts, which forms the basis for the entire coal and oil hydrogenation, was thus opened. Shortly thereafter it was shown that certain other oxide catalysts, as MoO_3 and WO_3, could also be used, because in the processing of products containing sulfur they are automatically transformed into sulfides.

Such catalysts were successfully used in the processing of tar in January 1925. A product as clear as water and free of oxygen, consisting largely of gasoline, was produced in one operation and without any coking whatever from Oppau brown coal generator tar. This proved the ability of these sulfur-proof catalysts to split higher molecular substances into low molecular, in addition to their high activity in hydrogenation.

The first experiments in hydrogenating tars were made with very low product partial pressure, below 1 atm at 200 atm total pressure. In later large scale experiments, in which thruput and partial pressures were necessarily increased, the catalysts showed rapid deterioration of their activity, caused by the deposition and condensation of high molecular substances on the surface of the catalysts These phenomena made it necessary to subdivide the process into two stages, the liquid phase and the vapor phase. In the liquid phase, the higher boiling, or high molecular, products are split into middle oils with boiling points of about 325-350° C by finely distributed catalysts, which are then further processed over fixed catalysts in the vapor phase.

The further development of the vapor phase catalysts then led, by way of Mo-Zn-combinations, to our first operating catalyst 3510, consisting of Zn-Mg-molybdate, and which proved to be very robust, both chemically and mechanically, while the very active Mo-Cr

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Besides systematic experiments in testing the most varied substances for their suitability for catalytic pressure hydrogenation the necessary conditions with respect to temperature and duration of heating for the most active Mo-oxide catalysts were determined in extensive common experiments with the Mo-laboratory and plant at Bitterfeld.

The development of highly active sulfides was further pursued, together with the production of these oxide catalysts, which are transformed into sulfides in the high pressure converter. This led to catalyst 5058, end of 1938, which consists of pure wolfram-disulfide and is produced by decomposing ammonium-sulfo-wolframate in an H_2-atmosphere.

The development of catalysts for the vapor phase was largely terminated with 5058, a maximum activity had been attained. Compared to 3510, 2 to 3 times as much gasoline was produced per hour with a fixed volume of catalyst, besides being able to work with a temperature lower by about 100° C, and the gasification losses were considerably smaller.

In order to use 5058 in mass production, the dry catalyst powder had to be compressed into cylindrical shapes 10 mm in diameter, instead of the former method of forming from a paste and then drying. With 5058 so produced, 3510 could be replaced for all but a few special purposes.

However, 5058 could no longer keep up with the demands for higher anti-knock gasolines in the processing of certain paraffinic raw materials because of its strong hydrogenation effect.

For this purpose, the co-called diluted catalyst 6434, developed in small scale experiments in the meantime, could be used. It consists of 90% Fullers earth treated with HF and 10% WS_2. It has at least the same splitting activity as 5058, but hydrogenates less strongly and produces higher anti-knock gasolines.

Its sensitivity to O_2 and N_2 combinations at first reacted against its general use. This necessitated the splitting up of the vapor phase into 2 stages, a prehydrogenation (saturation) stage, in which an extensive removal of O_2 and N_2 combinations takes place with the least splitting, and a benzination stage in which the purified middle oil is split into gasoline. This method is used in all hydrogenation works today, in which 6434 is generally used in the second stage, while in the first stage 5058 is partly being replaced by catalysts poorer in wolfram.

The development of catalysts poorer in wolfram was forced upon us by the war, which cut off the supply of wolfram. In protracted experiments we succeeded in finding catalysts 7846 and 7846W, which, although they require a somewhat higher temperature than 5058, are equal or even superior to it in prehydrogenation in spite of their considerably lower Mo or W content respectively. These catalysts consist of activated alumina with about 10-25% Mo-or W-sulfide and some Ni.

The combination 5058 + 7846 W/6434 has already been successfully used in Leuna, Pölitz and Scholven and will shortly be introduced in Gelsenberg, Wesseling, Brüx and Blechhammer.

The complete replacement of 5058 by 7846 has been deferred, for the time being, to avoid a possible drop in production during the war.

In the processing of middle oils from brown coal L.T.C. tar, Brabag also uses 6434 in the first stage.

Increased H_2 pressures offer further possibilities to save Mo and W. In small scale experiments, for example, petroleum middle oils could be transformed into gasoline with catalysts containing no Mo or W whatever.

The above mentioned excellent refining effect of the prehydrogenation catalysts has also found application in the refining hydrogenation of L.T.C. gasoline, cracked gasoline, raw benzol, kerosene, diesel oil, raw naphthaline, raw paraffin and lubricating oil. A special method for the production of paraffin and lubricating oil has been developed for brown coal tar in the TTH process.

The high concentration of active catalyst substance in the vapor phase permits the absorption of H_2 to the extent that the character of the feed stock, still retained to a large extent after the liquid phase hydrogenation, more or less disappears in the vapor phase, as shown in the following table:

H_2 Content in $gH_2/100\ gC$

	Petroleum	Brown Coal L.T.C. Tar	Bitum. Coal Coking Tar
Feed Stock	13.5	11.8	6.2
Distillation Middle Oil	15.0	12.1	7.7
Liquid Phase " "	14.5	13.0	9.5
Vapor Phase gasoline, strongly hydrogenated	17.9	17.6	17.0

The following table shows the strong refining effect in the vapor phase compared to the liquid phase:

Hydrogenation of Brown Coal L.T.C. Tar.

	Distillation Mi-Oil	Liquid Phase Mi-Oil from Coking Tar Residue	Vapor Phase Return Run Mi-Oil
Spec. Grav. @ 15°C	0.935	0.860	0.815
Aniline Point °C	+23	+18	+46
Boiling Range °C	195 - 325	195 - 325	185 - 295
% Phenols	24	5	0.3
% Sulfur	1.0	1.1	0.07

Even though the character of the raw materials more or less disappears in the vapor phase, there still exists a distinct relation between the character of the gasoline, particularly its anti-knock quality, and the feed stock, especially if weaker hydrogenating catalysts are used, as shown in the following table:

Auto-Gasolines From Various Raw Materials.

Feed Stock	Auto-Gasoline	
	Spec. Grav.	Octane Number
Middle Oil from: Paraffin	0.680	45
Petroleum, mixed base	0.722	64
" , asphalt base	0.728	67
Brown Coal L.T.C. Tar	0.734	65
" " Liquifaction	0.735	66
Petroleum Cracking Residue	0.745	74
Bitum. Coal Liquifaction	0.745	74
" " High Temp. Tar	0.748	75

The character of the hydrogenation products is further dependent upon operating conditions, such as temperature, pressure and the nature of the catalysts, which offered us the possibility of fitting the quality of our products to the rising demands.

Aromatization was developed in the first years of hydrogenation, by means of which, with the use of catalyst 3510 at temperatures above 500° C and high product partial pressures, anti-knock auto gasolines containing aromatics were produced, although with a somewhat reduced yield. This process was used in America for the processing of naphthenic petroleum middle oils and heavy gasolines. In Leuna, also, a certain amount of aromatization gasoline was made to improve the hydrogenation gasoline before the introduction of catalyst 6434.

The development of an extraction process with propane and SO_2 made it possible to obtain pure toluol from gasolines containing aromatics.

The further development of aromatization catalysts for 300 atm led, by way of activated charcoal-Fe-W, eventually to 7019, consisting of activated charcoal soaked in Cr-and V-oxide. It was used in Ludwigshafen before the war for producing aromatic high performance aviation gasoline from bituminous coal liquifaction middle oils. The mass production of these CV_2b-gasolines was taken up in Scholven, Gelsenberg and Politz after the war started. (This catalyst was later replaced by K534-535-536).

At 700 atm. other catalysts based on Fuller's earth (Bleicherde) can be used for aromatization. Gasolines produced by these catalysts from bituminous coal liquifaction middle oils at 700 atm. are somewhat poorer in aromatics than at 250 atm. By using special H_2-poor feed stock, such as pitch middle oil, Welheim produces VT 706, a gasoline similar to CV_2b, by this method.

The thermodynamic equilibrium between aromatic and naphthenic hydro-carbons is by far closer to the naphthenes under normal hydrogenation conditions, i.e. at temperatures of 400-500° C and pressures of 200-300 atm, and even more so at 700 atm. Low pressures and high temperatures favor the formation of aromatics. With a W-Ni catalyst 5615 developed in Leuna naphthenic gasolines were transformed into gasolines rich in aromatics at 50 atm. and 485° C. This process was temporarily used in Welheim.

The low pressure, however, has this disadvantage, that the catalyst may not last as long as in other hydrogenation processes because of polymerization of insufficiently hydrogenated products. This difficulty with sulfidic catalysts could only be overcome by using very low product partial pressures requiring disproportionally large quantities of H_2.

Based on the American hydro-forming process, Ludwigshafen developed the DHD process, which, at 20 to 50 atm, uses an alumina-molybdenum oxide catalyst 7360, which is periodically regenerated by burning in air. This process has this advantage, that it may supersede present hydrogenation processes as required and may also be used for dehydrogenating gasolines of other origin, such as petroleum stright-run gasolines.

It is natural that naphthenic-aromatic gasolines give better yields in the DHD process than paraffinic. Special catalysts, working at 700 atm have, therefore, been developed, producing especially high yields in naphthenic-aromatic gasolines, which, to be sure, do not yet represent high performance fuels, but which can readily be transformed into such by the DHD process.

If the DHD process is combined with a process already yielding products rich in aromatics, such as aromatization or a preceding first DHD stage, special products rich in aromatics can be produced, from which pure aromatics, such as toluol, can be produced by distillation.

The qualities of aviation gasolines produced in bituminous coal hydrogenation by the use of various vapor phase processes are summarized in the following table:

Aviation Gasolines From Various Processes of Bituminous Coal Hydrogenation

	Benzination E.P. 136°C	Benzination E.P. 155°C	Aromatization 300 Atm.	Aromatization 700 Atm.	Benzination + DHD	Aromatization + DHD
Spec. Grav./15°C	0.729	0.730	0.806	0.780	0.785	0.844
Parts to 100°C, Vol.%	64	57	30	38	50	42
End Point °C	136	153	165	165	165	165
Composition: Paraffin, Vol. %	38	40	15	20	26	6
Naphthene " "	55	52	35	41	24	11
Aromatics + Olefins Vol. %	7	8	50	39	50	83
Anti-Knock: Total Gasoline MM Oct. No.	75.5	73	80	79	84.5	92
Total Gasol. + 0.12% Pb. MM Oct. No.	92	91	91	91	94.5	100
Total Gasoline RM Oct. No.	--	75	89	90	94	104
Residual Gasol. (without aromatics) MM Oct. No.	--	--	65	69	75	72

Reel 129
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U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T 191

Discussions on March 26, 1943 in Leuna
The N 10 Material

Participants: Drs. Pier, Simon, Becker, Donath, Rank, Schappert, Raichle, Dinkler, and representatives from Blechhammer, Gelsenberg, Pölitz, Scholven, Wesseling and the Materials Testing Department at Leuna.

Dr. Pier first gave a brief review of the development of heat exchanging in the liquid phase. In Leuna, paste was heat exchanged ~~in stall 32~~, in Scholven heat exchange was unimportant, because of the cheap coal, in Politz heat exchange was urgently needed, because coal was expensive, and 1 heat exchanger was therefore in use; heat exchangers have become urgently necessary in Blechhammer because of the high thruputs.

The difficulties with the N 10 material are important in connection with heat exchangers, because of the reduction on the preheater load produced by them.

Mr. Schappert has presented tables which show the heat balance in the different plants.

Load on Preheaters at Different Hydrogenation Plants

	Scholven	Welheim	Wesseling	Nordstern	Politz	Upper Silesia
Thruput, t/h	24	33	46	36-20	40	70
Gas inlet, m^3/h	30,000	20,000	30,000	31,000	33,000	62,000
Heated to, °C	430	437	418	430-490	425	425
Heat of react. 10^6 kcal/h	4.8	4.5	7.0	7.2	8.0	13.0
Max. temper. of circul. gas, °C	590	570	560	560-595	595	600
Heat to be added, 10^6 kcal/h	8	8	11.5	9.8	10.6	19.4
% in heat exchanger	45 (1)	70 (3)	65 (2)	35 (1)	55 (1)	52 (3)
% in preheat.	55	30	35	65	45	48
No. of hairpins	24	25	18	30	21	33
Wall Temp. in unencrusted preheater: outside	478	495	488	482	480	530
inside	465	480	457	470	468	504
Wall temp. in encrusted preheater: outside				560	535	554
inside				535	505	536

Mr. Schappert discussed the fifferent ways of reducing the preheater load on the strength of the above data:

1). Alterations in the proportion of the different grades of coal paste and increasing its concentration. Politz has already carried this through: they have raised the concentration of the thick paste from 51 to over 54% and reduced its amount from 26 to 18 t.; the concentration of the thin paste was raised from 38 to 41%, and its amount increased from 43 to 52 t. The thick paste passes through the preheaters only, the thin paste only through heat exchangers. The resistance has been found to be increasing. The temperature was lowered by about 10°.

2). The use of cold paste might result in a reduction in temperature of 21° ~~(on the assumption of 7 t/h).~~ Gelsenberg has been introducing about 2 t/h for about one year. Scholven can add no cold paste, because its coal has deteriorated to such an extent, that additional increases in load are no longer permissible. Addition of larger amounts of cold paste has been postponed because the available pumps can not handle additional amounts.

3). The addition of a third (gas) heat exchanger.

4). Increasing the diameter of a converter might permit lowering the temperature by 60°.

5). Reducing the amount of gas, e.g. in Blechhammer from 62,000 to 50,000 m^3/h may permit a further reduction of the load.

By using all the methods the maximum flue gas temperature may be reduced from 600 to 540° and some 12 hairpins might be eliminated. The addition of a fifth converter in Blechhammer required the use of 150 t. of iron and a saving in 12 hairpins and a reduction in energy consumption.

The availability of space in Blechhammer, Nordstern and Politz for the addition of a fifth converter in the stall must be looked into.

The following table shows that but little of the reaction space is at present used for heating:

	Preheater outlet thermocouple 44	Total heat of reaction	Heat of reaction in 1st converter	% of reaction space used for heating
Gelsenberg	22.0-22.3	5.6	2.7-3.4	13
Pölitz	21.4-22.2	5.1	2.7-2.6	20
Blechhammer	22	9.7	5	25

Mr. Koch has stated that in addition to the former faults of the N 10 material, the reduction in resistance to deformation, brittleness has been encountered. Duration of condition of strain, temperature and hydrogen have brought about a grain separation. After 2 years of stress at 520° inside temperature, the damage becomes evident. True, the damage caused no surprise. The damaged pieces are not destroyed and can be recovered. After rehardening they can be put to additional two-year use.

Lowering the temperature by 10° doubles the life of the tubes. Any incrustations formed must be frequently removed. Improvements in N 10 are not possible because of shortages in materials, but the C and V contents should be lowered and the Cr content somewhat increased within the limits of the experimental error. This will reduce the creep resistance.

In addition to difficulties caused by faults of material, Pölitz and Gelsenberg are handicapped by crust formation. They form in Pölitz at 17 - 19.4 mv, and have about the same composition as in Gelsenberg, but with less material from the hairpins in it. The crust in Gelsenberg contained about 75% Fe. Three different layers can be readily observed in Gelsenberg; even the inside layer contains some material from the hairpins. Coal constituents are present in decreasing amounts towards the inside (titanium from the coal and the catalyst).

	Ruhr coal	Bayer mass	$FeSO_4$ $7H_2O$	Gelsenberg inside crust	outside crust
Iron: Titanium	51.1	8.1:1	90:1	66:1	350:1
Iron to coal		0.5	0.25		

No agreement was reached on whether these figures indicate a predominating effect of one constituent over the rest. Bayer mass is excluded because of its small iron content, which may not be entirely permissible, because all the components may take part in the sedimentation. The "lip" found in Leuna has been mentioned.

Pölitz on the strength of their experiments holds sulfigran responsible for the deposition, since it is supposed to cause a precipitation of iron at 150°. The suggestion was therefore made to add sulfigran behind the preheater, but the danger of chlorine corrosion prevented them from doing it.

Dr. Pier wished to know whether there was any danger of diffusion, in view of the presence of tube material (Cr) in the crust. Mr. Koch considers this impossible at a temperature of 500°.

Other means of saving tube material were discussed.

Pölitz blows through the vertical pipe line. No fears are entertained, because nothing more happens than when strong wind blows around the stall. The formation of ripples in the upright pipes indicates a weakening of the tubes.

Dr. Pier stated that operations must be carried out at the highest pressure possible.

Attention was called to the fact that direct low temperature coking would reduce the load on preheaters. Dr. Pier has not permitted himself to be convinced by this, and it was outside the scope of the discussion to go into it in greater detail. Dr. Donath would discuss it in greater detail later at night; it became impossible to arrive at any agreement.

When discussing the load reduction by a reduction of the amount of gas used, Dr. Peukert told of his observation, that when the amount of gases was reduced, the temperature inside the converters would rise if the same concentration of solids in the HOLD is to be obtained.

In this case, however, the suggestion made earlier by Mr. Peukert was discussed; it concerned increasing the length of time the charge stayed in the converter when reducing the amount of gas, which results in a better utilization of asphalt as has been done for years in Leuna. Dr. Peukert let Dr. Pier tell him, that he considered this observations to be of the utmost importance, altho before expressing his opinion he told me in private, that this was his own opinion (which is mentioned here in case of any later patent claims).

In conclusion, Dr. Pier made a suggestion, to operate one stall in a way to have the first converter act as a preheater. One such test has been in operation in Gelsenberg for half a day. The temperature could be reduced by about 2 mv. but other results (primarily yields) are as yet unavailable.

/s/ Becker

W.M. Sternberg
12/19/46

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U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-192

KCBraun
12/26/46

DEVICE FOR LOW TEMPERATURE CARBONIZATION OF CARBONACEOUS SUBSTANCES.

German Patent No. 699707,

Class 10a, Group 26_{01},

21 Dec. 1935

Issued to

I.G. Farbenindustrie, A.G. Frankfurt/Main

By

Dr. Mathias Pier, Heidelberg,

Dr. Albert Pross, Gelsenkirchen,

Dipl. Ing. Karl Goetze, Ludwigshafen, and

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The processing of oil and asphalt containing residues from pressure hydrogenation of coal and other carbonaceous substances is of greatest importance, but very difficult.

The most varied methods have already been proposed. For example, these usually viscous and sticky residues have been decomposed into oils and insoluble residues in stills and low temperature carbonization kilns of special construction, wherein the feed, for example, was treated in a thin layer on a heated base.

These processes are generally applicable where the processing of residues free of asphalt is concerned. With residues containing asphalt, however, very sticky masses are formed with increasing oil removal. These stick to the base and greatly hinder the conveyance of the material and the heat transmission thru the walls of the device and eventually stall the moving parts of the device, as e.g. the spirals of the kilns, etc. The proposals made to date are, therefore, not suited to the processing of residues containing asphalts.

It has now been found that the decomposition of the above mentioned residues containing asphalts into oils and insolubles may be accomplished very simply and without interrupting operations, if they are carbonized in a revolving drum containing variously shaped milling elements and provided with partition walls with attached flights, either inclined or at right angles to the axis of the drum. The drum is heated to the extent required to distill the oil without material decomposition and the asphalts are largely transformed into oils with little gas or coke formation. Deposition of the residue on the walls as well as obstruction of moving parts is practically eliminated in this process.

It has also been shown that in the use of this device a detrimental splitting of the oils in the feed material may be avoided, so that these may be recovered without material change in their boiling curves and used as pasting oil, hydrogenation feed, extraction media for solid carbonaceous materials, or for other purposes. The insoluble residues produced have a fine grained, non-sticky composition, so that they may be used without further treatment as pulverized fuel, for example.

It is of advantage to slope the revolving drum slightly. In order to avoid the formation of any deposits on its wall or to remove any thin crust immediately after formation, it has been proved to be advantageous to revolve the drum at given intervals during operations at such a high speed that a distinct milling effect will ensue. This milling effect is caused by the milling elements being carried upward on the drum wall by the rapid revolution, which then drop into the drum to loosen any deposit that may have formed. This will also prevent the milling elements from sticking together, which might be possible under certain conditions because of the nature of the feed stock.

Sub-dividing the drum by inclined partition walls or partition walls with attached flights at right angles to the longitudinal axis makes it possible to suit the treatment of the feed stock to its composition and the progressive oil extraction. The joints in the kiln walls are suitably formed in the shape of carrier flights. The partition walls must, of course, enable the material to be processed to move along readily and for this purpose must have suitable openings, which, however, must not be so large that the milling elements will pass thru them to the next processing chamber. This makes it possible to use more or differently shaped milling elements in the first stages of oil extraction than in the succeeding ones.

At times it is advantageous to give the milling elements a rotating motion by mounting suitable inserts, arranged longitudinally, on the kiln wall. This will give a good heat distribution and heat utilization. The milling elements may, for example, be conveyed in this fashion from a zone of low heat consumption into a zone of high heat requirement.

For the carbonization of coal, oil shales, etc, kilns with partition walls perpendicular to the axis, which permit the feed stock to be conveyed along, but hold back the milling elements, have already been used. However, these devices are not suited to the processing of oily residues from pressure hydrogenation or pressure extraction, because these substances would bake to the walls during carbonization. This drawback is eliminated when carrier flights or partition walls inclined to the kiln axis are used.

The attached sketch, which represents a longitudinal cross-section, shows the device in detail:

(a) represents a revolving kiln approximately 8 m long x 1.5 m dia., slightly sloped towards the discharge end, abt. 2.5%. The kiln is sub-divided into 2 chambers (a') and (a") by the inclined partition wall (c). The first of these (a') takes up about 2/3 of the total kiln space. It contains a total of about 5 tons of milling elements (b), consisting in the first chamber of about 60 brick shaped and about 65 spherical shaped steel elements. In the second chamber there are about 10 brick shaped and 30 spherical shaped elements. The stock is continuously fed at (d). The residue is discharged thru the end chamber (e), where it is picked up by the flights (f), which dump it into the chute (g). Steam enters at (h) in a direction counter to the movement of the stock. The oil vapors formed and the gases from the asphalts are discharged at (i). The kiln is heated by the gases generated in the fire box (k) by the coke dust from the kiln. The fuel gases enter the kiln jacket at (l).

The kiln turns at 14 R.P.M. At intervals of about 1 hr. the speed is about doubled for a few minutes. The temperatures inside the kiln are held to 500-550°C. The thruput is 600-800 kg/h with a steam consumption of about 350 kg.

In the processing of a residue from the pressure hydrogenation of bituminous coal, containing about 60% oil with 12% asphalt and abt. 40% insolubles (including 33% ash), an oil was obtained, at almost 90% yield, whose boiling range was approximately the same as that of the heavy oil contained in the feed. The asphalts were transformed up to 70% and more into oil.

Patent Claim.

A device for carbonizing residues containing oils and asphalts from the pressure hydrogenation of coals, tars, mineral oils, etc. or the residues containing oils and asphalts from the extraction of solid carbonaceous substances, particularly coal. This device consists of a revolving drum, subdivided by partition walls and containing suitably shaped milling elements, with openings provided between the sub-chambers for the passage of the feed stock but not for the milling elements, characterised by partition walls inclined or arranged perpendicularly to the longitudinal axis of the drum, in which latter case they are provided with carrier flights.

T-192

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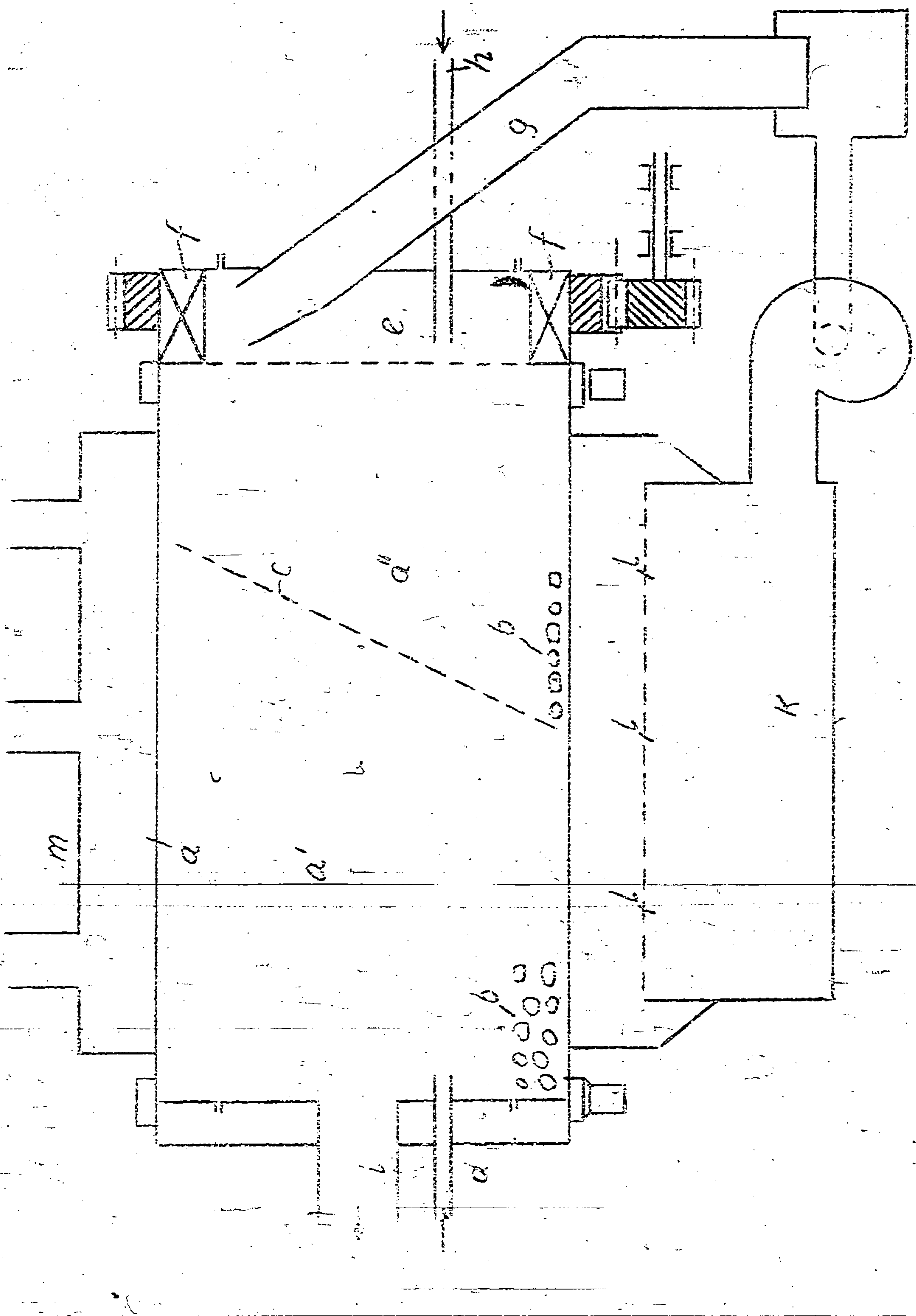
GERMAN PATENT 669707



GERMAN PATENT 669707

U. S. BUREAU OF MINES T-193
HYDRO. DEMON. PLANT DIV.

KCBraun
12/20/46

PRESSURE HYDROGENATION OF COAL OR SIMILAR SOLID CARBONACEOUS SUBSTANCES.

German Patent No. 656364

Class 12o, Group 1_{05}

19. May 1933

and

German Patent No. 675957,

Class 12o, Group 1_{05}

4. Aug. 1935

Issued to

I.G. Farbenindustrie, A.G. Frankfurt/Main.

By

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DRP 656364

Process for Producing Liquid Hydro-Carbons from Coal by Pressure Hydrogenation.

It is already known that the residue from the pressure hydrogenation of dry coal or coal mixed to a paste with oil may be separated into oil and insolubles by a thermal or mechanical treatment, e.g. filtration, centrifuging, or carbonization. It is of importance to industry that the processing of the residue be done continuously. However, such a process, e.g. centrifuging, is feasible only with hydrogenation residues still containing considerable quantities of coal not decomposed in the pressure hydrogenation. With residues containing only small quantities of undecomposed coal, in which there are solid particles of various sizes, continuous processing is difficult or even impossible.

It has now been found that these disadvantages may be avoided, if the coal, particularly brown coal, is mixed to a flowing paste with oil and pressure hydrogenated in the presence of a finely distributed catalyst until the solid particles contained in the hydrogenation residue are reduced to a uniformly small particle size, under 10 microns, and the hydrogenation residue is then continuously centrifuged, possibly with the addition of a diluting medium. The difference in the particle size should not exceed 7 microns. The time required for reaction depends upon operating conditions and the character of the feed substances. It is determined by the definite goal to obtain a particle size of less than 10 microns. In any case, the reaction time required is longer than usual, namely longer than that required for maximum yield in liquifaction products. When using an effective catalyst in quantities of 2% to 0.01%, for example, it may require 1/2 to 2 hrs.

For working the process, brown coal, for example, coarse grained or finely pulverized, is soaked in or sprayed with acid as hydrochloric, sulfuric, nitric, sulfonic, acetic, or formic acid. The quantity of acid used is properly such that the basic active constituents in the coal are either fully or partly neutralized. Acid above this amount is to be avoided. The coal may also be washed with acid and filtered, dissolving the soluble ash constituents. Before, during or after the acid treatment the coal is mixed with finely ground catalytically acting substances or soaked in a solution of catalytically acting compounds. Most suitable for this purpose are the elements of the 2nd to the 8th groups, e.g. Mo, Cr, W, V, or preferably in the form of their compounds, e.g. oxide, phosphate or sulfide. Zn-oxide, Zn-sulfide, as well as Co-sulfide and Fe-sulfide, for example are particularly suitable. Halogen combinations, such as Ni-iodide or organic halogen compounds may also be used as catalysts, either alone or together with the above named metals or metal compounds. The catalysts may also be used with carriers, such as active carbon, activated silicic acid, carbonization coke, or Fullers Earth (Bleicherde).

The coal so prepared is then made into a paste with an oil properly originating from the same coal, particularly middle or heavy oil, and, together with H_2, conveyed successively thru a gas fired preheater and a reaction vessel, in which latter it may remain 1-2 hrs. at a reaction temperature of 350-500° C.

All the products of reaction are conveyed, for the purpose of separating the oil from the residue, to a separating vessel, in which a temperature equal to the reaction temperature or 20, 50 or 100° C lower is maintained. If, for example, the temperature in the separator is appreciably lowered, corresponding portions of the oil vapors from the gases drawn off at the top, particularly those of heavy oil, are condensed, keeping the hydrogenation residue sufficiently fluid to be drawn off at the bottom of the vessel with the solid coal constituents. In this process it is generally not necessary to add diluting media before the separation of the hydrogenation residue into its constituents. If, on the contrary, the temperature in the separator is nearly equal to that in the reaction vessel, it may be necessary to add thinning oil to the hydrogenation residue, such as heavy oil derived from the same coal by pressure hydrogenation or carbonization. Middle oil or mixtures of middle oil and gasoline may also be used. The separation of the solid from the liquid constituents of the hydrogenation residue is done in centrifuges operating continuously. Centrifuges best suited for this purpose are disk (Teller) centrifuges with conical inner wall, in which the solid particles thrown against the outer wall are continuously conveyed thru slots or by means of spirals thru nozzles mounted in the drum wall, or removed from the drum by flights in a planetary motion. The liquid oil particles run off continuously thru an opening in the upper end of the drum. This oil may be used for pasting fresh coal after separating the low boiling constituents, such as middle oil.

In order to avoid any interruption in the continuous operation of the centrifuge, which is of the utmost importance for the economy of coal liquifaction, the hydrogenation process must be continued so long that the particles of coal in the hydrogenation residue not transformed into oil are largely of uniformly small size, below 10 microns. Apart from soaking the coal in acid, this condition may be attained by returning the residue from the pressure hydrogenation of coal to the reaction vessel, preferably mixed with fresh coal paste. The reaction feed may also be conveyed thru several reactors arranged in series. Other methods to obtain a hydrogenation residue best suited to continuous centrifuging, characterized by small and uniform particle size, and which will effect a lengthy reaction period, may also be used. The mean size of the coal particles not transformed into oil in the above described process is about 1 to 5 microns.

Example I.

Middle German brown coal is finely ground and sprayed with sulfuric acid (10% concentration), so that the basic coal constituents are neutralized. The coal so prepared is then soaked in a solution of ammonium-molybdate (0.5% MoO_3 based on dry coal) and then dryed to a water content of 1-2%. The coal is then mixed into a paste with the same quantity of heavy oil derived from the same coal by pressure hydrogenation and, together with H_2, is heated @ 200 atm. to 450°C in a gas fired preheater, from which it is conveyed to a reactor, where it remains 1 hour. The products of reaction are then conveyed to a separator held at 350° C, from the bottom of which the hydrogenation residue, consisting of heavy oil and solid particles, is drawn off, while the lower boiling oil constituents, together with the hydrogenation gas, are withdrawn at the top. 95% of the carbon contained in the coal is transformed into largely liquid constituents. The hydrogenation residue produced in this process contains 25% solids, consisting largely of ash and little carbon, and 75% heavy oil boiling above 325° C. The mean particle size of the solid constituents is 2 microns. This hydrogenation residue is then diluted with 25% of an oil boiling above 325°C and derived from pressure hydrogenation of brown coal and centrifuged in a continuous disk centrifuge with conical inner wall. The centrifuge residue contains 50% solids. The centrifuge oil is free of solid substances and is used as pasting oil for fresh coal. The hydrogenation residue is then freed of its oil constituents by low temperature carbonization with steam at a temperature of 500° C.

Example II.

Finely ground brown coal is drenched with a solution of ammonium-molybdate and made into a paste with a heavy oil derived from the same coal in the proportion of 1:1. The paste is then conveyed thru a gas fired tube preheater at a pressure of 250 atm and then thru a widened reaction vessel, where it remains for 1 hr. at a reaction temperature of 460° C. At the end of the reactor chlor-benzol or ethylene-chloride is added in such an amount that the chlorine contained in the coal paste in the reactor = 0.15%. The products of reaction then go to a separator, from the upper end of which the low boiling products and H_2 are withdrawn, while the hydrogenation residue is drawn off the bottom. This residue consists of 30% solids and 70% of oil boiling above 325°C. The particle size of the solids is about 3 microns. The hydrogenation residue is then diluted with 30% of an oil boiling above 325° C and derived from the same coal, and centrifuged in a continuous disk centrifuge with conical inner wall. The centrifuge residue contains 50% solids. The centrifuge oil is free of solids and is used as pasting oil for fresh coal. The decomposition of the carbonaceous substance in pressure hydrogenation - 96%.

Patent Claims.

#1. - Process for the production of liquid hydro-carbon substances from coal, particularly brown coal, made into a flowing paste with oil, by pressure hydrogenation in the presence of finely distributed catalysts, characterized by hydrogenating the coal under pressure so long that the solid constituents in the hydrogenation residue will have attained a uniformly small particle size, below 10 microns, and then centrifuging this residue, if necessary with the addition of a thinning medium, in a continuously operating disk centrifuge with conical inner wall.

#2. - Process according to Claim #1, characterized by using a feed coal previously prepared with acid.

#3. - Process according to Claims #1 and #2, characterized by returning the hydrogenation residue to the reaction vessel.

DRP 675957

Process for the Pressure Hydrogenation of Coal or Similar Solid Carbonaceous Substances.

In order to convert raw coal into a condition suitable for hydrogenation under pressure it must first be properly prepared. For example, the raw coal is first dried, then ground and freed of ash to facilitate the processing of the residue. Then catalysts are added and it is made into a paste with oil. Furthermore, the residue produced in pressure hydrogenation must be freed of its solid constituents, so that its oily constituents may be utilized, by diluting it with a lighter oil and then either filtering or centrifuging it. The oil constituents may then be used as pasting oils for fresh coal, after first removing the thinning medium, if necessary.

These cumbersome treatments can be greatly simplified by this invention by thoroughly mixing the oily residue produced in the pressure hydrogenation of coal with ground coal with water added to it, or by itself in the presence of water, then separating the water together with the ash, followed by a suitable treatment of the remaining mixture of H_2 under pressure at an elevated temperature in the presence of catalysts. The simplest method is to grind the coal with water and then mix it with the oily residue. But the water may also be added after grinding, or the residue may be added earlier in the process.

The following is a typical example:

Precrushed coal is mixed with enough water that the mixture can be pumped. The amount of water may vary between 50 and 200% of the coal, depending upon the nature of the coal. This mixture is then finely ground in a tube or a vibrating mill. The resulting coal-water paste is then mixed with residue produced in the pressure hydrogenation of coal, consisting of oil and solid particles in a suitable device, such a a kneader or a continuous spiral mixer. The amount of residue used corresponds approximately to that of the coal, by weight. The residue is preferably added in stages during the kneading. In this kneading operation the water contained in the coal paste, together with most of the ash suspended in it, is separated and then drawn off. The kneading operation, which takes only a few minutes, depending upon the character of the coal, may be appreciably accelerated by the addition of tetrahydronaphthaline, benzol, aniline, higher alcohols, etc., which increase the capacity of the coal to absorb oil and decrease its capacity to absorb water. The separation of the water by kneading may also be accelerated by the use of heat and, in certain cases, vacuum. Suitable additions, such as electrolyte, will also facilitate the separation of oil and water or of water and ash.

The paste obtained by this treatment consists of oil and finely ground coal, poor in ash, which is now heated to the reaction temperature, 350-600°C, and conveyed, together with H_2, under a pressure of 50 to 500 atm or more, thru one or more reaction vessels. After leaving the reaction vessel the products of reaction are decomposed by fractionated cooling and/or distillation.

The pressure hydrogenation residue used is produced, for example, in such a manner that the coal paste is conveyed thru the reaction vessel and the resulting product to a separator. A fixed liquid level is maintained in this separator and the temperature is adjusted so that the gasoline and middle oils pass off with the hydrogen, while the heavy oil with the high boiling oil constituents and those constituents not separated in the preparation remains liquid and is drawn off the bottom of the separator and used for kneading.

If the pressure hydrogenation takes place in the presence of catalysts, the coal may be ground with a watery solution or suspension of catalysts, such as ammonium-molybdate, zinc-oxalate, iron salts, etc. Acid, such as hydrochloric, sulfuric, nitric, etc. may also be added to the water, which will facilitate the deashing on the one hand and promote the catalytic effect in the pressure hydrogenation on the other. But a watery, alkaline solution may also be used, which will favorably influence the coal catalytically, with the simultaneous use of iron salts, for example. The catalyst may also be added to the coal-oil paste before the pressure hydrogenation in the form of finely ground metallic compounds, either with a carrier or in soluble form.

A double advantage is gained by the process described in this invention:

1. The coal is de-ashed in the simplest manner, and

2. The hydrogenation residues containing inorganic matter and undecomposed coal can be profitably utilized without a troublesome processing by filtration or centrifuging.

Although it has already been proposed to make a thin slurry of coal and water and mix it with oil for de-ashing, in this invention the coal is kneaded with water and an oily hydrogenation residue containing solids, wherein no de-ashing of the coal and even less a de-ashing of the residue itself could be counted on.

The surprising advantages achieved by this invention can neither be obtained by the known processes for dewatering of moist fuels, wherein these are mixed with ash-free oils, such as liquid products of hydrogenation, and then either heated to temperatures above 200°C at pressures over 200 atm, or centrifuged, or pressed out. A utilization of the coal hydrogenation residues, which will save their cumbersome processing, combined with a simultaneous de-ashing of the coal, can not be obtained by this process.

Patent Claims.

#1. - Process for the pressure hydrogenation of coal or similar solid carbonaceous substances, properly in the presence of catalysts, characterized by mixing the coal ground either by itself or with water, in the form of a watery slurry or paste, with the oily residue containing solids obtained in the pressure hydrogenation of coal, by separating the water containing ash and by returning the remaining coal-oil mixture to pressure hydrogenation.

#2. - Process according to Claim #1, characterized by using a coal ground with a watery solution or suspension of catalytically acting substances.

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-194

KCBraun
12/23/46

PROCESS FOR SEPARATING OILS FROM MIXTURES WITH SOLID SUBSTANCES

German Patent No. 550157,

Class 12o, Group 1,

26. Oct. 1927,

and

German Patent No. 630965,

Class 12o, Group 1_{05},

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Issued to

I. G. Farbenindustrie, A. G., Frankfurt/Main.

By

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No. 630965:
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DRP 550157

In many technical processes, particularly in low temperature carbonization, cracking and extraction of carbonaceous materials, as well as in the pressure hydrogenation of coals, tars, mineral oils, etc, larger or smaller quantities of products are produced, consisting of mixtures of oils and solid substances, such as carbonaceous residues, ash particles or other solid pollutions such as catalyst. It is often very difficult to separate these solids from the oils.

It has now been determined that the separation of these solid constituents from the oily products is appreciably facilitated, if the mixture is centrifuged with the simultaneous addition of liquids dissolving the oil and of wetting media, particularly in a watery, neutral or weakly alkalinic solution.

It is known that the decomposition of mixtures of solid and liquid substances difficult to separate, particularly if the latter are highly viscous, may be appreciably facilitated, if the mixtures are diluted with solvents for the liquid components. However, this generally requires considerable quantities of solvents whose subsequent separation is difficult and costly.

This disadvantage can now be largely avoided by adding to the solvents watery solutions of wetting agents, which form an emulsion with the added solvent and the oil to be separated, which, in turn, can be readily separated from the solid constituents in centrifuging. The saving of considerable quantities of solvents does not represent the only material improvement compared to the present process, but also the fact that it is possible to de-oil the solid substances to be separated fairly thoroughly, which is impossible with the use of solvents alone, because of the considerable quantities of solvents still adhering to the solid particles after separation.

It has also been proposed to separate naphthaline and anthracene from the oils containing them by emulsifying the oils with water in the presence of emulsifying media, in certain cases after the addition of solvents, and then separating the naphthaline or anthracene by filtration. Thus, the former process uses entirely different products, on the one hand. On the other hand it is not possible to obtain a satisfactory separation of the solids by centrifuging, because the solid substances are present in ultra-fine suspension due to preparation in colloid mills, etc. and do not possess the required differential in density.

It is also known that wet oil sludge may be de-oiled by centrifuging, after dilution with acidified water and solvents specifically lighter than water. However, this process can be used only for relatively light oils, but not for products such as heavy and highly viscous oils and residues produced, for example, in the thermal treatment of coal or oily materials, because the dissolving and emulsifying effect of such mixtures of solvents and water in many cases is only slight. In most cases, it completely fails, because the acidity of the water acts counter to the formation of an emulsion with such products. This disadvantage is also eliminated by the use of wetting agents such as nuclear alkylated sulfonic acids of aromatic hydrocarbons, cellulose pitch, saturated and unsaturated fatty acids and their salts, etc, particularly in watery, neutral, or weakly alkalinic solutions, which loosen the adhesion between the solid substances and the adhering oils. Furthermore, this process is not limited to the use of watery products, as in the known process, but feed materials practically free of water can also be used for de-oiling from the start, such as thermally treated coal, oil and tar products. And, finally, any kind of solvent, be it specifically heavier or lighter than water, can be used with this simplified process, contrary to the formerly known processes. The best solvents, in particular, are aromatic hydro-carbons, like benzene, toluene, xylene, or hydro-aromatic, like tetra-hydro-naphthaline, or those containing chlorine, as chloroform or methylene-chloride, or even such rich mixtures as brown or bituminous coal tar oils, their fractions or hydrogenation products.

If, for example, a product obtained from the pressure hydrogenation of certain brown coals is centrifuged by itself, no separation whatever will result in many cases. But, if about 30% of one of the aforementioned solvents is added, together with about 100% of a watery solution of a wetting agent, a separation will often be obtained with ordinary centrifuges, even when cold. The simultaneous use of wetting agents will not only save considerable quantities of solvents, compared to other processes, but the residue will be much more thoroughly de-oiled in centrifuging, because the specifically heavier wetting agent solution will displace and wash out most of the oil still adhering to the residue by the action of centrifugal force. In order to remove the last traces of the oil in the residue, it is often proper to centrifuge the residue repeatedly with the addition of solvents and wetting agents. Various solvents may be used.

In many cases, particularly in the processing of pressure hydrogenation residues, such as bituminous coal residues rich in asphalts, it may be advisable to add the solvent to the material to be processed, as long as this is hot, 150°C and above, because the solid constituents are more easily separated at high as well as at low temperatures. This method is particularly recommended with residues having a high solidifying point (Stockpunkt). It has also been shown that under certain conditions certain changes, such as are caused by condensation, for example, take place in the cooling of some mixtures stored in heat, and that substances containing hydro-carbons stored in heat, which have first been cooled off and possibly solidified, are very often more difficult to dissolve than substances treated immediately with the solvents while they are hot, before cooling. The solvents may be also heated before mixing with the substances to be treated. In the processing of pressure hydrogenation residues the hot product coming from the converter under pressure is preferably cooled to the temperature at which it is desired to expand it (entspannen) by the injection of the cold or slightly preheated solvent. In this way, no heat is lost in special cooling devices and a considerable saving of heat is obtained. This also favors the easier pumping of the products so diluted and a thorough mixing of the solvent and the product to be treated. It has also proved of advantage to use pressure centrifuges, which may be directly connected to a high pressure vessel.

Under certain conditions a part of the adhering oil may first be removed by centrifuging without adding a solvent to the mixture to be separated. If necessary, the oil may be forced out of the centrifuge by washing it out with water. The centrifuging of the oily residue may then be continued with the addition of benzene and a wetting agent. In this case it is proper to construct the centrifuge so that the added solvent can readily mix with the residue. A residue almost completely free of oil is thus obtained.

Example I.

The oily residue obtained from the pressure hydrogenation of brown coal is mixed with 30% of a brown coal tar fraction of 250-300° C boiling range and the same quantity of water, to which a little sodium isopropylnaphthalinesulfolate has been added, and the mixture is centrifuged at 100° C, readily separating it into 3 layers, consisting of residue, water and oil.

Example II.

The sludge obtained in the pressure hydrogenation of brown coal is mixed with half its weight of heavy gasoline, adding 0.25% olein and 0.25% ammonia. The mixture is then centrifuged at 90-95°C and washed with a little heavy gasoline. A practically pure oil is obtained and a residue with 18% benzol-soluble constituents, consisting largely of added heavy gasoline. These can be practically completely removed from the residue, if it is washed with a hot 0.25% solution of watery olein (or turkey-red oil) ammonia solution until the washing liquor appears clear and free of gasoline. The residue will then contain only 1.4% benzol-soluble constituents. The oil contained in the washing liquor is separated by neutralization. If the separated washing liquor is again mixed with the proper quantity of ammonia, it may again be used in the washing process with the same effectiveness.

Patent Claims

Process for the separation of oils from mixtures with solid carbonaceous substances as produced in the pressure hydrogenation, cracking, carbonization, etc, of coals, tars, mineral oils, etc, characterized by centrifuging the mixture to be separated with the simultaneous admixture of liquids having good dissolving power for the oils to be separated and of wetting agents, particularly in a watery, neutral or weakly alkalinic solution.

DRP 630965

It is already known that the sludge obtained in the pressure hydrogenation of coal may be decomposed into oil and solids by centrifuging. However, it has been shown that it is generally impossible to obtain an oil entirely free of solids by a continuous process, particularly with large thruputs.

It has now been found that this disadvantage can be overcome by continuously centrifuging the oily residue obtained in the pressure hydrogenation of coal in stages, if need be with the addition of thinning media or refining agents, so that the oil obtained in the first stage will contain a certain amount of solids, properly about 2%, which are then separated from the oil in the second stage.

To carry out this process, continuously operating centrifuges are properly used, such as plate centrifuges with conical inner wall, where the solid particles thrown against the walls of the drum are continuously removed from the centrifuge by spiral screws.

The hydrogenation residue to be processed is mixed with thinning agents, such as heavy oil, middle oil, or low boiling hydro-carbons, properly produced by pressure hydrogenation from the same coal in the desired proportion, for example, 1 part residue to 0.2 to 0.5 parts of thinning agent and then conveyed to the centrifuge. In the first stage, for example, a sludge containing 15 to 25% solids, which has already been mixed with 0.2 to 0.5 times the amount of thinning agent, is centrifuged in large quantities so that an oil still containing 3 to 5% solids is obtained. This oil is then completely freed of solids in a second stage, also with a large thruput. The separation in the second stage may be done in plate centrifuges with conical drum walls, in which the residue is discharged thru a nozzle located at the apex of the cone. The centrifuging takes place at 80 to 200° C, depending upon the viscosity of the oil, preferably at 130 to 150°C.

It is of advantage to return the residue from the second stage, which still contains about 30% solids, to the first stage in order to separate the oil adhering to the residue. The residue produced in the first stage in considerable quantities and containing about 45-55% solids, is properly freed of its residual oil constituents by carbonization with flushing gases (Spülgasen), such as steam, nitrogen, etc.

It is furthermore of advantage to regulate the pressure hydrogenation so that the solids contained in the residue will show a uniform particle size.

This process has this advantage, that the hydrogenation residue of the coal is continously decomposed into its constituent parts by centrifuging, even with large thruputs in a given time.

Example.

A residue obtained from the hydrogenation of brown coal, consistin of 25% solids, principally ash, and of 75% heavy oil boiling above 350°C, obtained by pressure hydrogenation from the same coal, and centrifuged at 140°C in a plate centrifuge, in which the centrifuge residue is discharged thru nozzles mounted in the drum wall. With a thruput of 3000 l/h, 1040 parts of residue consisting of 50% solid constituents and 1960 parts of a centrifuge oil containing 4.2% solids are obtained. The centrifuge oil is centrifuged in a second stage having a capacity of 4000 l/h, from which 3400 parts of a pure oil entirely free of solids and 600 parts of centrifuge residue containing 30% solids are obtained. This centrifuge residue is returned to the first centrifuge stage, while the residue from the first stage is subjected to a low temperature carbonization with steam at 500° C. 95% of the oil contained in the first stage centrifuge residue is hereby recovered.

If, however, the hydrogenation residue is centrifuged in one stage, the capacity is limited to about 1500 l/h in order to obtain pure oil and a concentrated solids residue at the same time. The technical and economic advantage of multistage centrifuging according to this invention, compared to single-stage centrifuging, is best illustrated in the following considerations:

In order to produce the 4000 l/h feed material for the second stage centrifuge, two centrifuges of 3000 l/h each are required in the first stage. These 6000 l produce roughly 4000 l for the second stage centrifuge. These 4000 l yield 3400 l pure oil. If these three centrifuges are operated in parallel, only 1500 l/h each, or a total of 4500 l/h, can be processed to obtain the same purifying effect. This invention, therefore, will enable the processing of 6000 l, compared to 4500 l for the known process, in a given time to produce the same quantity of pure oil.

Patent Claims.

1. Process for the separation of oils from mixtures with solid substances, particularly from the residues obtained in the pressure hydrogenation of coals, tars, mineral oils, etc, by means of continuously operating centrifuges, characterized by stage-wise centrifuging of the mixture, if need be with the addition of thinning or refining agents, so that the oil obtained in the first stage still contains a small amount of solids, which are separated from the oil in the second stage, in which, if desired, the residues obtained are returned to the first stage.

2. Process according to Claim 1, characterized by subjecting the residue from the first stage to heat by the use of flushing gases (Spülgasen), if desired.

T.OM. Reel 129
Reference a-4
Frames 69 - 79

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-195

July 14, 1943

DIRECTIONS FOR ACCOUNTING IN HYDROGENATION PLANTS.

All accounting must conform to rules and regulations made by the individual economic units. However, inside these rules, accounting must be adapted to the process, the costs of which are being studied. We have presented here an accounting method developed for hydrogenation plants.

1. Tasks of Accounting.

The volume of accounting depends on the results expected from it. The less it is expected to produce, the briefer the calculations, and vice versa. The following requirements are usually made for the hydrogenation accounting:

I. Possibility of evaluating the principal cost factors (yield, consumption of hydrogen, etc). Load upon the different accounting stations.

II. Separate accounting for the production from different raw materials when used together (coal, tar, etc.)

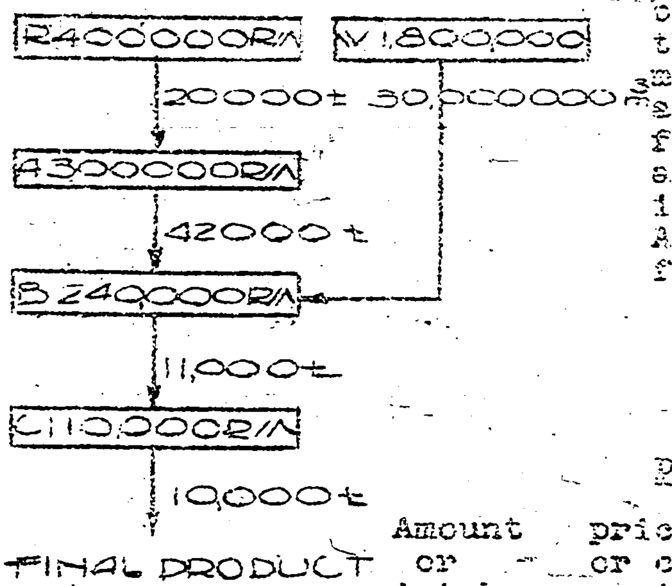
III. Separate accounting for the production of different finished products during a simultaneous production (gasoline, diesel oil, fuel oil, etc.).

2. Solving Specific Accounting Tasks.

We will first show solutions of simple cases of accounting tasks mentioned above. Conditions here have been greatly simplified, keeping clear, however, the important features. The total costs are presupposed to be distributed among the actual hydrogenation operations (accounting stations). This is the duty of the accounting office at the plant and is not further discussed, because done by the usual accounting methods. It is advisable to distribute among the different accounting stations the costs of the auxiliary materials (catalysts, etc.) as well as the costs of operation. On the other hand, the cost of hydrogen must be computed separately (as the efficiency of the production, independent of the hydrogenation) without distributing it among the accounting stations (in this case the converter stalls) because different grades of coal may, under special conditions, consume different amounts of hydrogen with the same thruput. A special information on the costs of hydrogen is also advisable because of the large proportion of these costs in the total costs. The same applies also to the hydrogenating gas. We shall below consider only three accounting stations (A, B and C) and hydrogen (W), as the efficiency of the plant outside the actual hydrogenation.

I. One single raw material, one final product, no changes in stock of intermediates.

FLOW SHEET



An especially simple case is presented in the adjoining flow sheet. The numbers in the different quadrangles are the costs per month, in RM., of the raw material, hydrogen and the different accounting stations, the remaining figures are the amounts of materials and finished products in t/mo. (except in the case of hydrogen, in m^3/mo). Accounting can be readily made by following the scheme below.

	per month			per ton finished prod.	
	Amount or intake	price pre unit, or costs/ton input	RM	amount	RM
Raw material	20,000	20.-	400,000	2.000	40.-
Hydrogen, W	30,000,000	60.-	1,800,000	3,000	180.-
A	20,000	15.-	300,000	2.0	30.
B	12,000	20.-	240,000	1.2	24.
C	11,000	10.-	110,000	1.1	10.-
A+B+C+D = costs of production			2,450,000		245.-
Total	10,000	285.0	2,850,000	1.0	285.-

This accounting scheme permits one to see all the factors of importance in the calculation of production costs. The amounts and yield are subdivided into hydrogen, and the individual accounting stations. In addition, costs are calculated per ton of input or per m^3 of hydrogen. It is, e.g. immediately seen that when the cost of hydrogen is increased, this will be attributed either to a higher hydrogen consumption, or to a higher price for hydrogen. If so desired, costs may also be additionally subdivided (interest, energy, etc.) in so far as known for the individual accounting stations and for hydrogen. The requirement of 1-I, "possibility for evaluating the principal cost factors" is therefore largely met.

It has been found advantageous to purely formally change the above scheme, whenever the accounting must be subdivided among a larger number of raw materials, intermediates and finished products. We shall illustrate it on the above simple case in order to bring out the essentials, although it seems trivial in this case. The new presentation is done in four steps:

1-st step Recalculating the flow sheet of 1 t. of raw material (calculation of yield)

	per t. raw mater.	Total
hydrogen m^3	1,500	30,000,000
Input of A t.	1.00	20,000
" B t.	0.60	12,000
" C t.	0.55	17,000
Final product t.	0.50	10,000

Unlike the first case, the specific values have been calculated per ton of raw material, not per ton of the final product.

2-nd step Calculation of specific costs per cost of one ton of input and the price of hydrogen.

	Input, or m^3	Costs per t. of input (per 1000)	Costs, RM, per month
hydrogen	30,000,000	60.-	1,800,000
accounting station A	20,000	15.-	300,000
" " B	12,000	20.-	240,000
" " C	11,000	10.-	110,000
conversion costs			2,450,000

3-rd step Recalculation from steps 1 & 2 of conversion costs of 1 t. of raw material.

	Costs per ton input (or 1000 m^3 hydrogen)	Input per ton raw materials	Costs per ton raw materials.
hydrogen	60.-	1.500	90.
accounting station A	15.-	1.00	15.-
" " B	20.-	0.60	12.-
" " C	10.-	0.55	5.50
Conversion costs			122.50

Control: Total costs of conversion: 20,000 x 122,500 = 2,450,000 RM.

4th-step Computation of Production Costs.

This is done of the strength of: Production costs = raw materials + conversion costs; therefore

Raw material input			Conversion costs	Final products		
ton	RM/t	RM	RM	ton	RM/t	RM
20,000	20.-	400,000	2,450,000	10,000	285.-	2,850,000

The final results are the same as above. The reason why a scheme so simple in kind has been developed in great detail will be understood later. We will limit ourselves to stating now, that the first step, "computations of yields" is separated because usually carried out by the plant accounting office, instead of the main accounting office.

We may show the accounting of intermediates, which is frequently required on the sample discussed. (It may be needed for the evaluation of available stocks and sale of intermediates). Let us assume, that an intermediate product leaves the accounting station B (11,000 to/m) and must ~~be~~ accounted for; in this case the conversion costs at the station B must be computed, and the results can then be readily seen:

	RM	
Raw material	400,000	
Conversion costs W + A + B	2,340,000	
Value of the intermediate	2,740,000	for 11,000 ton or

$$\frac{2,740,000}{11,000} = 249.09 \text{ RM/t.}$$

Exactly the same results are obtained starting with the cost of the finished product and deducting the costs of the C step, that is the conversion costs required for the conversion of the B product into the finished product:

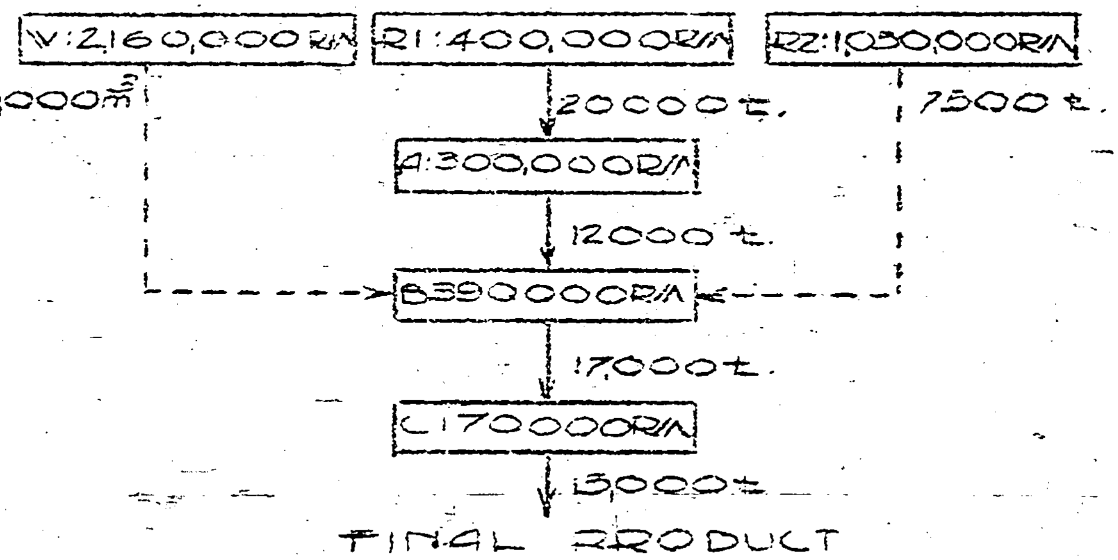
	RM	
Finished product	2,850,000	
Less conversion costs of the intermediate into the final product	110,000	
Value of the intermediate	2,740,000	for 11,000 t, or

$$\frac{2,740,000}{11,000} = 249.09 \text{ RM/t}$$

This important possibility of deriving the value of an intermediate from the final product is important, because in many instances this is the only possible way. (V III).

II. Different Raw Materials, Converted To-Gether

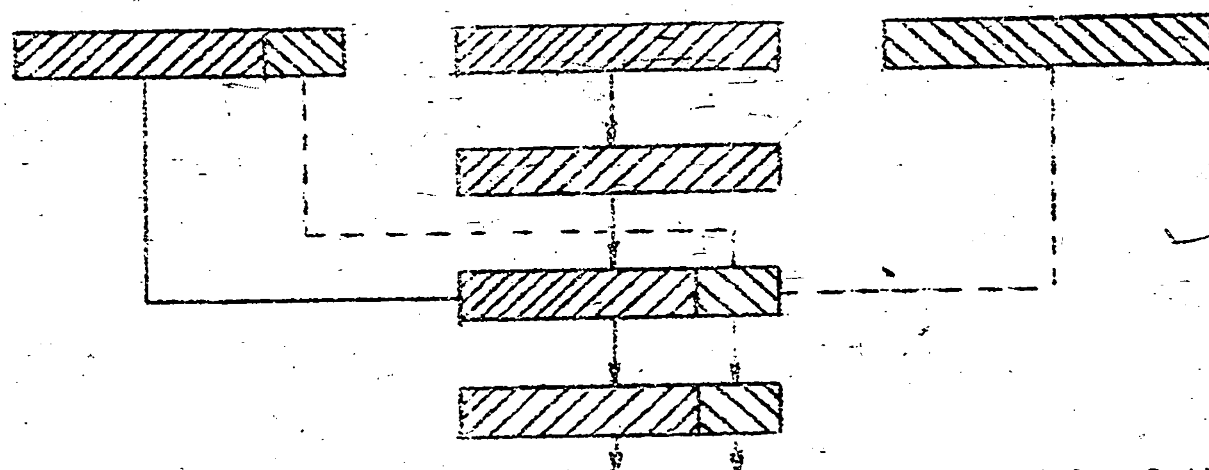
FLOWSHEET



Two raw materials are now used simultaneously, and one of them is introduced into step A, the other in the step B. We may first compute as in the first scheme.

	amount or input	per month Price per unit, or cost per t. input	RM	per t. finish prod. amount	RM
Raw material 1	20,000	20.-	400,000	1.333	26.67
" " 2	7,500	140.-	1,050,000	0.500	70.00
Total raw materials	27,000	52.73	1,450,000	1.833	96.67
Hydrogen, W	36,000,000	60.(1000)	2,160,000	2.400	144.00
A	20,000	15.-	300,000	1.333	20.00
B	19,500	20.-	390,000	1.300	26.00
C	17,000	10.-	170,000	1.133	11.33
Total, W+A+B+C			3,020,000		201.33
Total	15,000		3,370,000	1.000	298.00

However, the costs, 298 RM/t of the finished products are mixed costs, and it is very important to know the cost of the finished product from the raw material 1 and the raw material 2. This can be determined by finding the load of each of the raw material, i.e. the consumption of hydrogen, at each accounting stations. This is indicated in the flow sheet below by different crosshatching:



After such a separation, performing computations for each of the raw material becomes simple. It must however be emphasized, that in this case a correct distribution of costs is important. We will omit carrying out the individual computations, and make the computation as shown in the second scheme.

1-st step Computation of yields

t.	Raw material, 1 20,000 per/ton	Raw material 2 7,500 per/ton	Total (control)*
hydrogen m^3	1.500	800	36,000,000
input in A t.	1.000	-	28,000 (20,000?)
input in B t.	0.600	1.000	19,500
input in C "	0.550	0.800	17,000
fin. prod. "	0.500	0.667	15,000

* e.g.: 1500 x 20,000 - 800 x 7,500 = 36,000,000

2-nd step. Computation of specific costs/t input and hydrogen consumption.

	input, t, or consumption m^3	costs/t per t. input (or 1,000 m^3)	Costs RM/month
hydrogen	36,000,000	60.-	2,160,000
accounting station A	20,000	15.-	300,000
" " B	19,500	20.-	390,000
" " C	17,000	10.-	170,000
conversion costs			3,020,000

3-rd step <u>Conversion Costs Per Ton of Raw Material</u>

	costs per ton input, or 1000 m³	raw material 1 per ton		raw material 2 per ton	
		Input	RM	Input	RM
Hydrogen	60.-	1,500	90.-	800	48.-
Accounting Station A	15.-	1.00	15.-	-	-
" " B	20.-	0.60	12.-	1.00	20.-
" " C	10.-	0.55	5.50	0.80	8.-
Conversion costs			122.50		76.-

Raw material input

Control: 20,000 x 122.50 = 2,450,000
7,500 x 76.00 = 570,000
Conversion costs = 3,020,000

4-th step Computation of final costs

	Input of raw material			convers. costs	finished product		
	t.	RM/t	RM	RM	t*	RM/t	RM
Raw material 1	20,000	20.-	400,000	2,450,000	10,000	285.-	2,850,000
" " 2	7,500	140.-	1,050,000	570,000	5,000	324.-	1,620,000
Total	27,500		1,450,000	3,020,000	15,000	298.-	4,470,000

* calculated from the costs in first step
20,000 x 0.5 = 10,000
7,500 x 0.667 = 5,000

This computation gives directly the costs of the final product from the raw materials 1 and 2; the mixed cost (298.- RM/t) agrees with the one obtained under II. The labor of computation in this 4-th step is hardly greater than in the first scheme discussed, were one to make special computations for each raw material.

A variant of this method of computation can be obtained by using instead of a raw material an intermediate which has the same properties as the raw material 2, and will have the same conversion costs. However, the price of this intermediate is as yet unavailable, and it must first be evaluated. One may start with the helpful requirement, that the finished product obtained from this intermediate should have the same value, as the final product with the foreign raw material (in our case, therefore, 285.-RM/t). One may in this case simply calculate backwards, as follows:

	amount	RM/t	RM
Final product	5,000	285.-	1,425,000
Less conversion cost			570,000
	7,500	114.-	855,000

or, by introducing this computation directly into step 4:

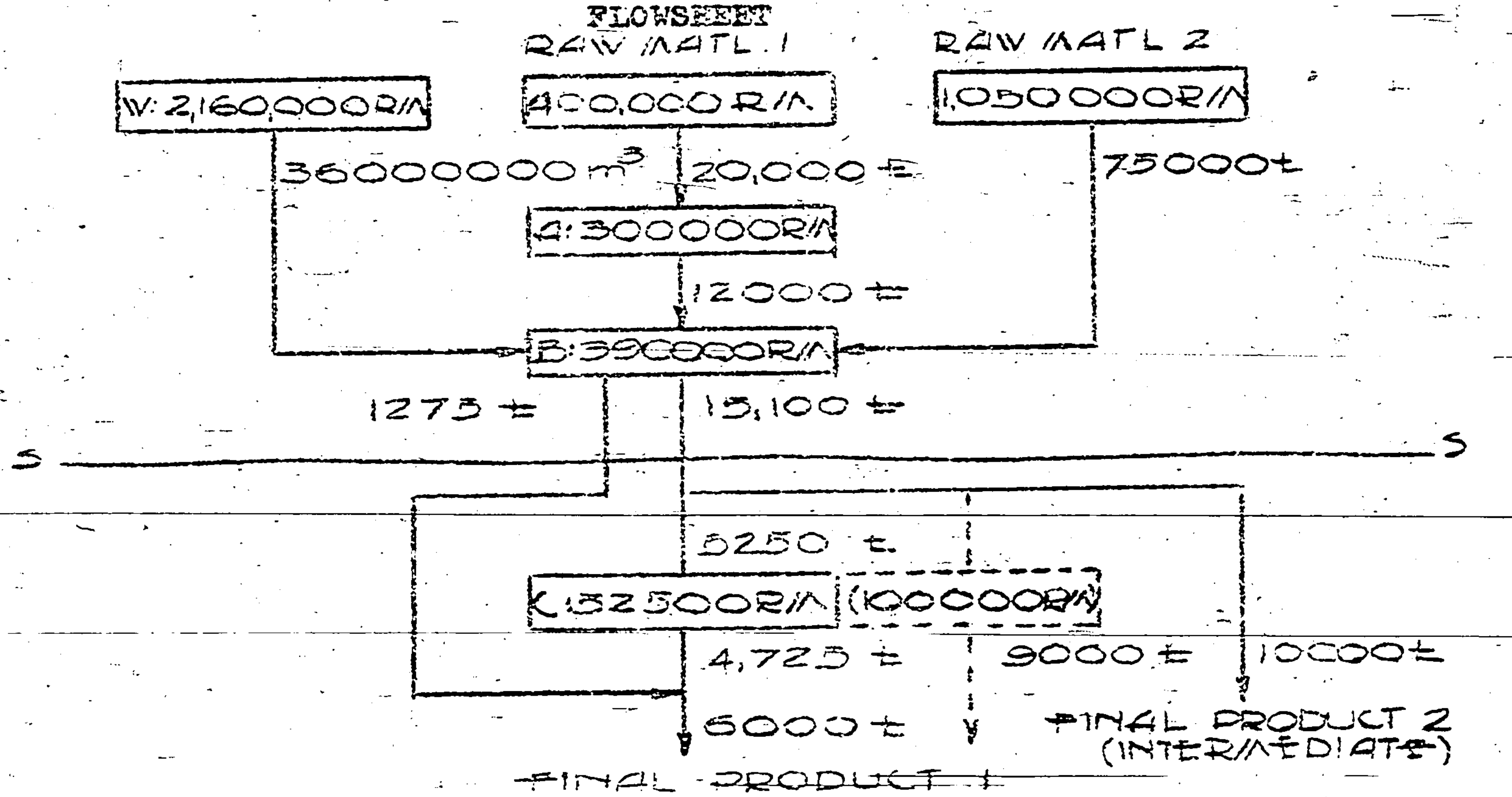
	Input			Conversion costs	Final product		
	t.	RM/t	RM	RM	t.	RM/t	RM
Raw mater. 1	20,000	20.-	400,000	2,450,000	10,000	285.-	2,850,000
Intermediate	7,500	114.-	855,000	570,000	5,000	285.-	1,425,000
	27,500		1,255,000	3,020,000	15,000	285.-	4,275,000

Computations for raw material 1 is performed in the usual way from left to right, and the final products cost of 285.- RM/t is obtained. The same final cost is assigned to the final product from the intermediates, and the value of the intermediate computed from right to left. The scheme may therefore be used directly for the introduction of costs of intermediates, and for their evaluation, with any number of raw products or intermediates present.

The requirement II: "Separate cost accounting for production from different raw materials when used to-gether" is therefore fulfilled.

III. Different Final Products with a Simultaneous Production or Evaluation of the Intermediates Obtained.

FLOWSHEET



It has been assumed, in the extension of the case II, that in the cost accounting station C 10,000 to of intermediate is routed out of the system and disposed of as a "final product" (e.g. B-middle oil as diesel oil; or crude gasoline as DHD feed). It is in addition assumed, and is actually frequently the case, that some of the products encountered in the station B have the properties of final products and are no longer led through C (e.g. pentane). We now shall determine the cost of the final product as well as of the intermediate.

This can not be done directly. We may try first to find the cost down to the line SS. They are:

	RM
Raw material 1	400,000
Raw material 2	1,050,000
Hydrogen	2,160,000
Accounting station A	300,000
Accounting station B	390,000
	4,300,000

1275 t of a product with the as yet unknown value of the final product 1, and 15,250 t of an intermediate, 10,000 t of which is taken out as the final product 2 are components of the above costs. The value of the second final product is also as yet unknown. A sum of costs of two different products must be divided into two parts, and this problem is indefinite, and can not give a single solution. A solution is obtained in the following way.

If the 10,000 t were not to be taken out, but converted into the final product, an additional amount of the final product would be obtained, and the costs at the accounting station C would be higher. This additional amount can be easily calculated as follows:

	actual, per month	per ton of input	recalculated to
Input into the account. station C	5.250	1	10,000
Final product 1 obtained from it	4,725	0.90	9,000
Costs at station C	52,500	10.-	100,000

The amount of the final product has increased by 9,000 t, the costs at the accounting station C by 100,000 RM; 10,000 t intermediate has not been detoured. (This is shown as a broken line in the flowsheet.) The figures given can therefore be readily recalculated for the case of only one single final product being formed, and obtain the cost as follows:

	per month			per t final product 1.	
	amount, or input	price per unit or cost per ton input	RM	amount	RM
Raw material 1, t.	20,000	20.-	400,000	1.333	23.66
" " 2, t.	7,500	140.-	1,050,000	0.500	70.00
total raw material	27,500	52.73	1,450,000	1.833	96.66
Hydrogen, W m^3	36,000,000	60.-	2,160,000	2.400	144.00
Station A t.	20,000	15.-	300,000	1.333	20.00
Station B "	19,500	20.-	390,000	1.300	26.00
Station C "	5,250	10.-	52,500	0.350	3.50
W + A + B + C			2,902,500		193.50
Final product 1 t.	6,000			0.400	
" " 2 t	10,000		4,352,500	0.687	290.75
Costs at the station C when processing 10,000 Final product 2 into 9,000 t product 1	10,000	10.-	100,000	0.667	0.67
Costs recalculated to product 1	15,000	296.83	4,452,500	1.000	296.83

We obtain thus the cost of 296.83 RM per ton of the final product 1 (mixed product from raw materials 1 and 2). It must be remembered, that the specific values per ton of the final product have been obtained by division by the re-computed production, i.e. 15,000. The final product 2 can now be readily obtained from the difference:

	amount	RM/t.	RM
Total production	16,000	272.-	4,352,500
incl. product 1	6,000	296.83	1,781,000
and product 2	10,000	257.15	2,571,500

The value of the second product is therefore 257.15 RM/t., and can also be found from the control, as follows:

1 t. of product 2 represents 0.9 t. product 1, therefore

$$0.9 \times 296.83 = 267.15 \text{ RM/t.}$$

deducting conversion costs at station C	10.0
	257.15 RM/t

It has therefore been found, that whenever more than 1 product is obtained at any station, the evaluation of the different products is indefinite and cannot be exactly solved. Evaluation may only be exactly

	per month			per t final product 1.	
	amount, or input	price per unit or cost per ton input	RM	amount	RM
Raw material 1, t.	20,000	20.-	400,000	1.333	28.66
" " 2, t.	7,500	140.-	1,050,000	0.500	70.00
total raw material	27,500	52.73	1,450,000	1.833	96.66
Hydrogen, W m^3	36,000,000	60.-	2,160,000	2.400	144.00
Station A t.	20,000	15.-	300,000	1.333	20.00
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$$0.9 \times 296.83 = 267.15 \text{ RM/t.}$$

deducting conversion costs at station C	10.0
	257.15 RM/t

It has therefore been found, that whenever more than 1 product is obtained at any station, the evaluation of the different products is indefinite and cannot be exactly solved. Evaluation may only be exactly obtained after the different intermediates have been convertered with known yields and coversion costs into the same final products.

The calculation shown above has still the disadvantage that the cost the final product 1 appear to be the mixing costs of raw materials 1 and 2. The separation may be made by the method indicated in II. It has been found advisable, however, to carry out the calculations in 4 steps. This is done below.

1-st step. Computation of yield

	Raw material 1	raw material 2	intermediate = final prod. 2	total Control*
tons	20,000	7,500	10,000	
Hydrogen m^3	1,500	800	-	36,000,000
Input in A	1.00	-	-	20,000
" B	0.60	1.0	-	19,500
" C	0.50	0.70	1.00	5,250
Final product	0.50	0.667	0.90	6,000

*control, e.g. for the final product:
0.50 x 20,000 + 0.667 x 7,500 - 0.90 x 10,000
10,000 + 5,000 - 9000 = 6,000

2-nd step. Computation of specific values of the inputs and the H_2 price.

	Input, tons, or consumpt. of H_2, m^3	Costs/to of input or/1000 m^3	Costs RM/month
Hydrogen	36,000,000	60.-	2,160,000
Station A	20,000	15.-	300,000
Station B	19,500	20.-	390,000
Station C	5,250	10.-	52,500
Conversion costs			2,902,500

3-rd step. Conversion costs/ton raw material (or final prod. 2, or intermediate)

	costs/ton raw mater. or 1000 m^3	Raw material 1 Input per ton	Raw material 1 RM	Raw material 2 per ton input	Raw material 2 RM	Intermediate = prod. 2 per ton input	Intermediate = prod. 2 RM
Hydrogen	60.-	1,500	90.-	800	48.-	-	-
Station A	15.-	1.00	15.-	-	-	-	-
Station B	20.-	0.60	12.-	1.00	20.-	-	-
Station C	10.-	0.50	5.-	0.70	7.-	1.00	10.-
Conversion costs			122.-		75.-		10.-

control: 122 x 20,000 + 75 x 7,500 - 10 x 10,000
= 2,902,500

4-th step. Computation of Final Costs

	Input			Conversion costs RM	Final product		
	ton	RM/ton	RM		ton	RM/ton	RM
Raw material 1	20,000	20.-	400,000	2,440,000	10,000	284.-	2,840,000
" " 2	7,500	140.-	1,050,000	562,500	5,000	322.50	1,612,500
Mixed costs	27,500	52.73	1,450,000	3,002,500	15,000	296.83	4,462,500
Intermediate (- prod. 2)	10,000	257.15	2,571,500	100,000	9,000	296.83	2,671,500
	17,500			2,902,500	6,000	296.83	1,791,000

The same prices have been found as previously, namely 257.15 for the final product 2, and a mixed price of 296.83 for the final product 1 which however is subdivided in this case into 284.-RM from the raw material 1 and 322.50 RM/t from raw material 2.

The scheme here shown can be readily applied to any number of raw materials and intermediates, provided they can be converted into one and the same product, the yield and conversion costs of which are known.

When this assumption is satisfied, as it is in most cases, requirement three is fulfilled, namely, of the "separate accounting for the finished products during their simultaneous production".

3. Practical Execution.

Suitable formulae can be conveniently used when actually carrying out the above computations. Emphasis must in this case be placed on having the formulae for the computation of yields to be carried out by the operating department agree exactly with the other formulae used in the calculation.

The possibility of subdividing the costs of the different raw materials and final products depends largely on the subdivision of the operating costs into the different operational groups (accounting stations). This must be taken into consideration during the practical execution of the accounting.

/s/ Pichler

W. M. Sternberg
12/24/46

DR. L. L. [illegible]

TOM Reel 129
Ref. 1,
pp. 675-769

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-196

Hydrogenation or Rhenish Brown Coal

Tests on hydrogenation of brown coal were undertaken because of the remarkable results obtained in Leuna, where no difference in the utilization of asphalt was found in the hydrogenation at 300 and 600 atm. A test run here showed definitely, that there was an equally great effect of pressure upon the Rhenish brown coal as upon the Elise coal (a high bitumen medium oxygen lignite from a deposit near the Leuna works; private communication of Dr. Hubmann. Translator).

A number of comparative tests were performed to learn conditions. The asphalt content of the HOLD was found to be only 2/3 as high when operating at 600 atm as at 200 atm. It has, on the other hand, been found, that the young, very high in oxygen Rhenish coal produces as much as twice the amount of asphalt during hydrogenation as does the Elise coal. Similar results have also been obtained earlier with the Senftenberg brown coal.

Iron catalyst was to be used, and for that reason different iron catalysts were studied, e.g. bog iron ore, the lauta and lux masses, as well as the Bayer mass. Here again striking differences in behavior could be found in comparison with the Elise coal. Three catalysts, arranged in the order of their activity with the Elise coal were the Bayer mass, the lauta mass and bog iron ore. The order was, however, reversed when hydrogenating the Rhenish brown coal. Naturally, these results apply only to the samples of catalysts tested. We may not say that the Bayer mass or the bog iron ore are better, because both these materials vary greatly in quality. Bog iron ore varies most, depending on its origin. Lauta mass, on the other hand, is very uniform in its activity. However, the above case permits one to see clearly the difference in the hydrogenation behavior of the two coals. Obtaining bog iron ore and the lauta mass was very complicated at the Wesseling plant, and it has been decided to use the Bayer mass, because exceedingly large amounts of it were at a very short distance from the plant. Anyway, the difference in freight is so great, that even a large excess of the cheaper substance became permissible. When the Rhenish coal is hydrogenated at 600 atm but with the same thruput, the same proportion of the catalyst, and at the same temperature, as the Elise coal at 200 atm, the asphalt content of the Rheinbraun HOLD is 50% higher than with Elise. Operating at a higher pressure permits, however, raising the temperature, which offers a way for the conversion of the asphalt.

Comparative runs at low and high pressures showed an other very surprising result. At 200 and 300 atm, no difficulties at all were found in the preheating, but a very strong, purely inorganic crust is formed in the preheater coil at 600 atm, in fact that crust formation was so strong that after operating for 24 days with a 10 mm coil, only a 2 - 3 mm wide channel was left open, and the coil became completely plugged up 3 - 4 days later. The deposit in the first fourth of the coil was slight, becomes then much greater, reached its full thickness in the middle, and then remained equally thick to the outlet.

The reason for the difference in behavior at 200 and 600 atm must surely be explained by the much greater degree of conversion of the organic material, and therefore also the decomposition of the inorganic constituents, producing thus the required conditions for the depositions inside the coil.

The catalyst was added in one run only after preheating, in order to slow down the conversion during preheating. Later experiments were conducted with a view of affecting the inorganic constituents of the coal by suitable additions to the coal.

The following procedure was adopted to obtain as nearly quantitative results as possible: All tests were run with the same thruput (1.0, referred to coal paste) and at the same temperature (23.3 mv) for 24 days. The coil was then dismantled, cut up, the deposit weighed and analyzed. The normal deposit consists almost entirely of Fe, CaO and CO_2. With the high-salt Hermine coal, washing with H_2SO_4 greatly reduced the formation of the deposit of salt, and the effect of neutralization with H_2SO_4 was tested in this case as well. We have found, that with a 50% neutralization the amount of deposition was reduced to 60%. Increasing the amount of sulfuric acid to 100% neutralization brought no further improvement, (with Hermine a reversal at 12%).

The effect of $(NH_4)_2S$ has been studied to get a connection with the tests in Ludwigshafen. It has been found in Ludwigshafen tests, that the addition of 2% $(NH_4)_2S$ to coal would avoid the formation of a deposit in the preheater. Leuna experiments disclosed a very slight effect of the addition of $(NH_4)_2S$, but it has been found, that the deposit was much more loose than without it, which offered the possibility that with a 70 times great flow the deposit in large scale units would be flushed out of the system. In addition, a favorable effect of $(NH_4)_2S$ was found on the utilization of asphalt, in that the asphalt content of the HOLD was reduced by 25%. The favorable effect upon the conversion of asphalt was highly desirable, but the addition of $(NH_4)_2S$ is very complicated, and it has therefore been tested whether the addition of elementary sulfur would have a like effect. It has been found, that the effect of addition of 2% of elementary S instead of $(NH_4)_2S$ was the same upon the asphalt conversion, but better upon the deposition inside the coil, by reducing its amount by 50%, while leaving its structure unchanged. Several objections to the use of elementary sulfur are justified: we know, that when oils are heated with sulfur, polymerization may be readily caused with the formation of tarry products. It may well happen, that the above mentioned favorable effect of sulfur upon the catalyst would outway its effect upon the oils. (Tests are at present run to find out whether by modifying the method of addition, still more favorable results could be obtained, as well as the optimum amount of sulfur to add).

The results of analytical investigation of the crust were interesting. The salt deposition from the Hermine - Henriette coal consisted principally of alkalies, CO_2, CaO, Al_2O_3, MgO and Cl, while the principal constituents from the Rhenish coal were, as already mentioned, Fe, CaO and CO_2. Neutralization with H_2SO_4 affects chiefly CaO and CO_2; the deposits then consist principally of iron. The addition of $(NH_4)_2S$ also results in an increase in the iron content, with a corresponding decrease in CaO and CO_2. The addition of S affects chiefly the proportion of iron, and results in the formation of a low iron crust, high in CaO and CO_2. When coal is neutralized, the alkali and alkaline earth humates are mostly decomposed, while the iron in the iron humate is probably present as a complex compound, which does not interact with the acid. The crust is presumably formed through the decomposition of the humates upon the hot coils. The neutralized coal contains principally iron humate, and in this case the crust will consist principally of iron, as well as of iron sulfide. In the not neutralized coal, calcium humate is also deposited, and breaks down into $CaCO_3$. One might perhaps assume the formation of FeS from iron humate at high concentration of S and H_2S at some temperature lower than the normal reaction temperature, with the production of a suspension in the oil, which will not become baked on the coil to a hard crust.

Should the opinion on the effects of neutralization and of the addition of sulfur be correct, they would become especially valid when the two causes are combined. The crust formation was actually reduced to 19% of the original, with a 50% neutralization and the addition of 2% S. It was even more loose in structure, than the one previously described. At first this method could not be considered very practical because of cost. The effects of additions were, moreover, not entirely satisfactory, and efforts were made to reduce the load on the coils by lowering the preheater temperature. The temperature was reduced from 23.3 to 2[illegible].0 mv, which still was technically permissible. With normal paste, and with no additions, the amount of deposition was greatly reduced, namely to 38% of the usual amount. Moreover, since this deposit was rather high in iron, conclusions were drawn on the greater effect of temperature upon the iron, than upon the calcium humates. The test showed the important effect of temperature, and explained the difference in results from those obtained in Leuna and Merseburg with respect ot the addition of $(NH_4)_2S$. No appreciable reduction was found in this case (8%), while in Leuna it was considerable. It became obvious, that with the better insolation in Leuna, the temperature was considerable lower in the preheater, than in the control tests. It became important to ascertain the effect of sulfur additions at lower temperatures. It was found to be nearly as great as expected, because the deposition was further reduced from 38% to 22%.

The tests have shown some of the factors which determine the formation of deposits of inorganic constituents during the hydrogenation of brown coal. Results are not completely satisfactory, in that the crust formation could not be entirely overcome. Experimental results are, however, less favorable than in large scale operations (lead bath preheater as against a gas preheater, velocity of flow of 8.3 cm against 5 m, 80% coal conversion against a maximum of 46%), and there existed a hope, that on a large scale the deposits would be kept at a permissible level, and the results obtained on a small scale tests had therefore to be tested under industrial conditions.

We shall not discuss the auxiliary equipment, because we were chiefly interested in conditions in the technical preheaters. The latter consisted of 17 ribbed hairpins 10 mm in diameter. Each hairpin was 17.8 m long. The heat exchange of the preheater outlet was obtained by passing hydrogen through two cooling columns, and the mixture of gas and paste entered the preheater at 8 mv. The preheater was gas fired, and was so operated, that the outlet temperature of the products was 21 mv. The hydrogen-paste mixture passed through the above mentioned cooling columns behind the preheater through a cooler to the catchpot.

The hourly thruput was 400 li. of coal paste and 400 m^3 of make-up hydrogen at 600 atm pressure. The solids content of the coal paste was about 47%. The first test was run with the usual coal paste, with no additions and lasted for 42 days of operations. As a result of trouble in auxiliary equipment, operations had to be suspended twice during that time; however, the interruption did not affect the results. After conclusion of the tests, all connecting bends between the hairpins were opened, and the thickness of the deposits measured. In addition, in order to obtain an accurate picture of the inside of the hairpins, one of the hottest hairpins was dismantled and sawed into pieces. The deposit was found to be rather uniform in thickness over the whole hairpin. For still closer study of the deposit, part of the ascending tube was completely cut through and the deposit determined quantitatively. An examination of the heater tubes disclosed a much more favorable picture, than obtained in small scale tests. When operating on a small scale, about 3/4 of the tubes had a uniform deposit, while in large scale run only the last third of the tubes had any important deposition. The thickness of the deposit was only one half that of the tubes in small scale tests, namely 1.35 mm. Quantitative estimation with deposits of such thickness is very uncertain, especially if it is very had, as in these tubes.

At any rate, a thin layer of iron sulfide is formed on the bare wall. When the crust above is being remove, the iron sulfide is removed with it. The error is the smaller the thicker the deposit. The weight of deposit on 1 meter of the length of the tube was 111 gram. Analysis showed it to consist of 95% iron sulfide. Such high iron content has never been encountered in small scale runs, the highest value obtained was 77% FeS.

Disregarding the uncertainties of the correct taking of the sample, we may explain the results by the predominant decomposition of the iron humates at low coal conversion. The addition of sulfur was found from small scale experiments to be particularly effective. A second test was therefore run in stall 11, in which conditions were kept unaltered except for the addition of 2% S to the weight of dry brown coal. Unfortunately, the run could not be made for the full 42 days, because of the necessity of closing down after 34 days when the cooling columns became plugged up. The tests could not be completed because of the difficulties in obtaining coal. The hairpin dismantled in the first test was replaced with one from the cold pass, which had practically no deposit. Dismantling after the second tests was done exactly as after the first. A very similar looking, but much slighter deposit was only 71% as thick as in the first test. The weight of the deposit, recalculated to the same time, was however 93%. The composition of the deposit was at first surprising, being practically identical with that obtained in the first run. (94% FeS in the second, 95% in the first test). It was believed from small scale tests that the amount of iron sulfide would be reduced, while the amount of lime would be increased. However, this apparent contradiction can be readily explained, when the conversion figures of coal are considered. The coal conversion in the pilot plant tests was very high, but was but 34% in the first large test, and 46% in test 2. Results in the pilot test were obtained for the total conversion of coal, on the large scale for only a partial conversion, namely the behavior of the readily convertible coal constituents. Were we to assume that with a low conversion only the more sensitive iron compounds enter the reaction, and that some of these are especially sensitive to temperature, and not affected by sulfur in their reaction mechanism, the picture obtained will naturally be very different at a high and at a low temperature, with only a partial reaction, in one case, and a complete reaction in the other. Should the more stable compounds follow regularities more closely, deviations produced by the more sensitive compounds will be less marked with a greater conversion. One could readily see from this consideration why it is impossible to avoid all crust formation by a combination of sulfur addition and neutralization.

It is important in large scale tests to be able to answer the question of further growth of deposit with time. The observation has been made in pilot test runs, that the thickness of deposits does not increase linearly with time, but that the growth is more rapid in the beginning, and then slows down. This was determined by taking the tube following the one with the maximum deposit and dismantling it as well. This tube has been used during both operation periods, and the deposit must have consisted of the sum of deposits during the two runs. The results showed, that the deposit has not become any larger, assuming that the two tubes could be considered completely analogous. The assurance would be greater if the tube immediately preceding the first were also studied. Leuna, Feb. 27, 1940.

No signature

W.M. Sternberg.
12/30/46

TOM Reel 173,
Pgs. 880-884

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-197

KCBraun
12/26/46

EXPERIMENTS TO DETERMINE THE SENSITIVITY TO NITROGEN OF CATALYSTS

June 1938, by Mohr & Simon

In a series of experiments the behavior of various catalysts towards nitrogen additions in the form of aniline was systematically tested. The injection feed was Elwerather gas oil, containing 0.002% N. The % N-additions in the following experiments include the N in the feed.

Tested were:

1). Fullers Earth (Bleicherde) treated with HF,
2). Synthetic Terrana, (6792)
3). Catalyst 6434 @ 200 atm.
4). " 6434 @ 600 atm.
5). " 5058,
6). Fe-W-Catalyst, (6719)

For increasing additions of N the decline in gasoline produced, compared to that produced without N, was determined.

I). HF-treated Fuller's Earth (Bleicherde) @ 600 atm.

N-addition in %	0.01	0.017	0.042
Production without N	0.33	0.37	0.40
" with N	0.23	0.12	0.1
Decline in production %	35	66	75

After N-additions were omitted the catalyst did not regain its original production.

2). Synthetic Terrana @ 600 atm.

The synthetic catalyst 6792 showed a decrease in production from 0.46 to 0.18, or 62% when 0.04% N was added. Another variation of the same catalyst with 3% CaO already showed a decrease in production from 0.23 to 0.15, or 35% when 0.017% N was added.

3). 6434 @ 200 Atm.

N-addition in %	0.017	0.062
Production without N	1.25	
" with N	0.55	0.6 with 1 MV higher temperature
Decline in production %	56	

An increase in temperature of 1.5 MV was enough to equalize an N-addition of 0.017%. With 0.062% N-addition the temperature had to be increased 2.5 MV compared to operating without N. At first the production of 1.2 was about as great as without an N-addition, but was gradually reduced to 0.5 in the course of 300 hrs.

4). 6434 @ 600 Atm.

N-addition in %	0.0017	0.0017	0.062
Production without N	1.2	1.1	1.1
" with N	1.0	0.64	0.32
Decline in production %	17	42	70

At 600 atm. the N-sensitivity was about as great as @ 250 atm. To equalize an N-addition of 0.062% an increase in temperature of 2.5 MV was required, the same as at 200 atm.

5). 5058.

N-addition in %	0.017	0.042	0.22
Production without N	1.2	1.25	--
" with N	1.15	0.75	0.55
" after omitting N	--	1.19	1.25
Decline in production	4	40	56

With an increase in temperature of 1 MV with 0.042% N, almost the original production could be obtained. No deterioration could be noticed up to this time.

6). Catalyst 6719 (Fe-W).

This catalyst showed no effect of the high N-addition of 0.22%.

Comparative Nitrogen Sensitivity of Various Catalysts.

Catalyst	% Decline from Original Production		
	0.017% N	0.042% N	0.22% N
HF-Fuller's Earth	66	75	--
6792, Synth. Terrana	35	62	--
6434 @ 200 atm.	56	--	--
6434 @ 600 atm.	42	65 (estim.)	--
5058	4	40	56
6719, Fe-W	0	0	0

The above figures indicate no appreciable differences between fullers earth, synthetic fullers earth and diluted catalyst. The addition of tungsten sulfide reduces the nitrogen sensitivity to small N-additions to some extent. The same effect is also produced by increasing the pressure with diluted catalyst.

Catalyst 5058 is almost insensitive to N-additions; only with N-additions 10 times as large as with 6434 does it show a decline in production equal to the diluted catalyst @ 200 atm. The insensitivity to N-additions of the Fe-W-catalyst is striking.

TOM Reel 180
Pp. 833-835

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-198

KCBraun
12/26/46

ARRANGEMENT OF GASOLINE CONVERTERS AND HEAT EXCHANGERS FOR VARIOUS CATALYSTS

27 September, 1937
by Dipl. Ing. Schappert.

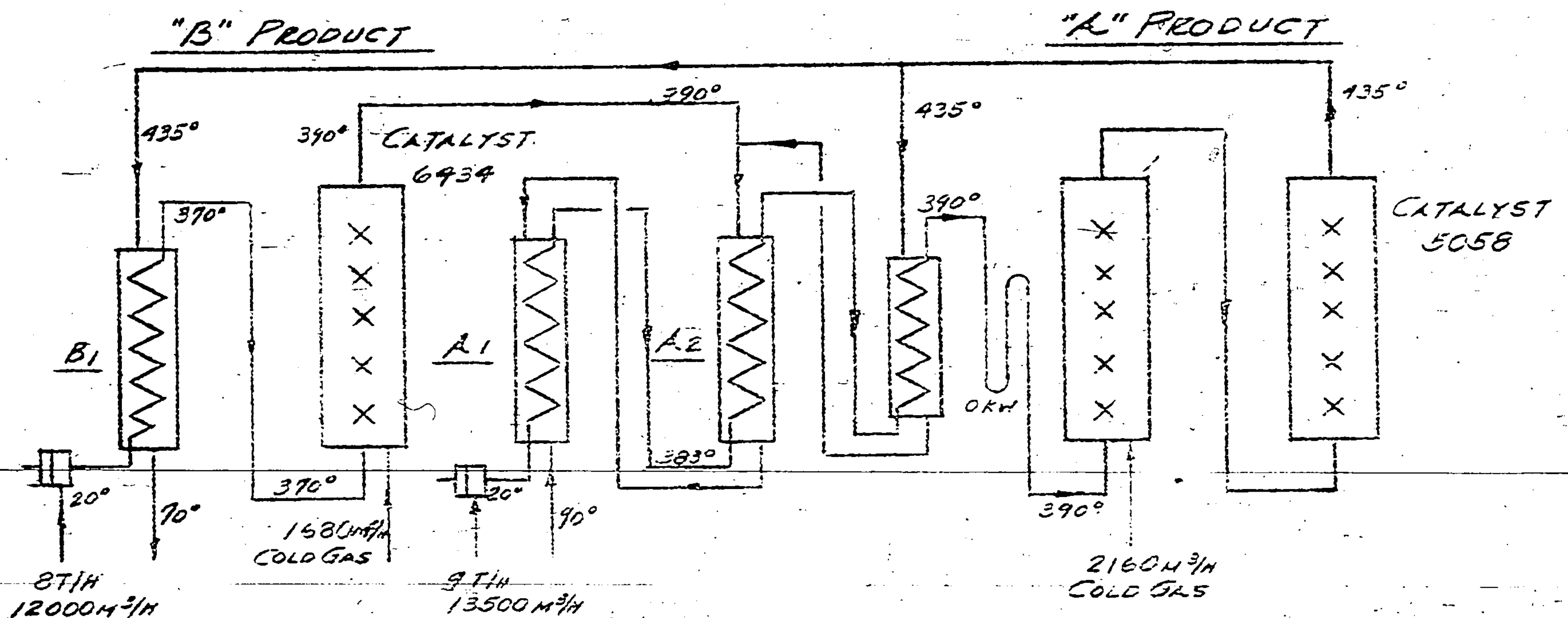
The arrangement suggested by D.I. Schappert for the combination of catalysts 6434 and 5058 in one stall, in which the "B" product is brought to the reaction temperature without a preheater, was tried out in 3 variations for its heat economy, compared to the present arrangement.

The various hook-ups are shown on the attached sketches.

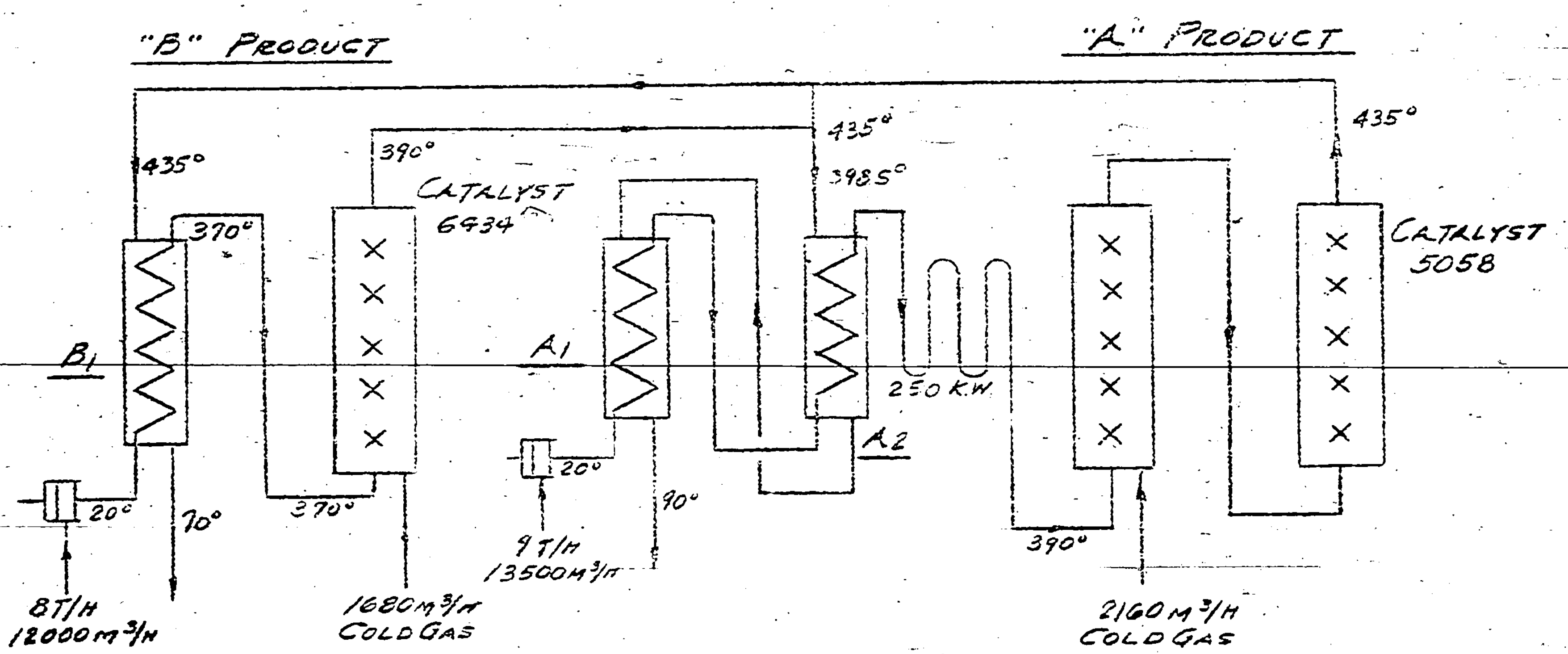
Results:

Arrgmt. 1.	3 normal and 1 small heat exchanger (in order to utilize the peak temperature). Additional energy required =	0 K.W.
Arrgmt. 2.	3 normal heat exchangers. Additional energy required =	250 K.W.
Arrgmt. 3.	3 normal heat exchangers. Additional energy required =	0 K.W.
Present Arrgmt.-	2 stalls, 2 heat exchangers, 2 electric preheaters. Additional energy required =	390 K.W.

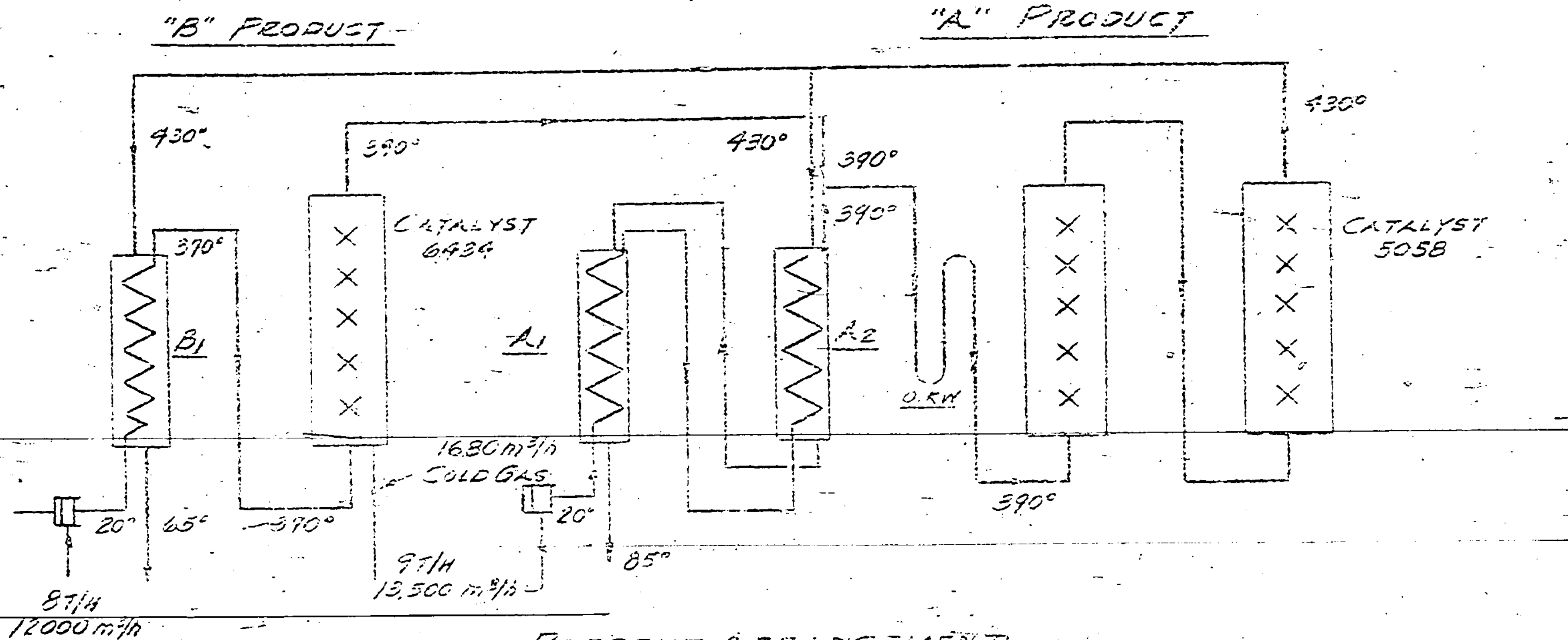
ARRANGEMENT 1



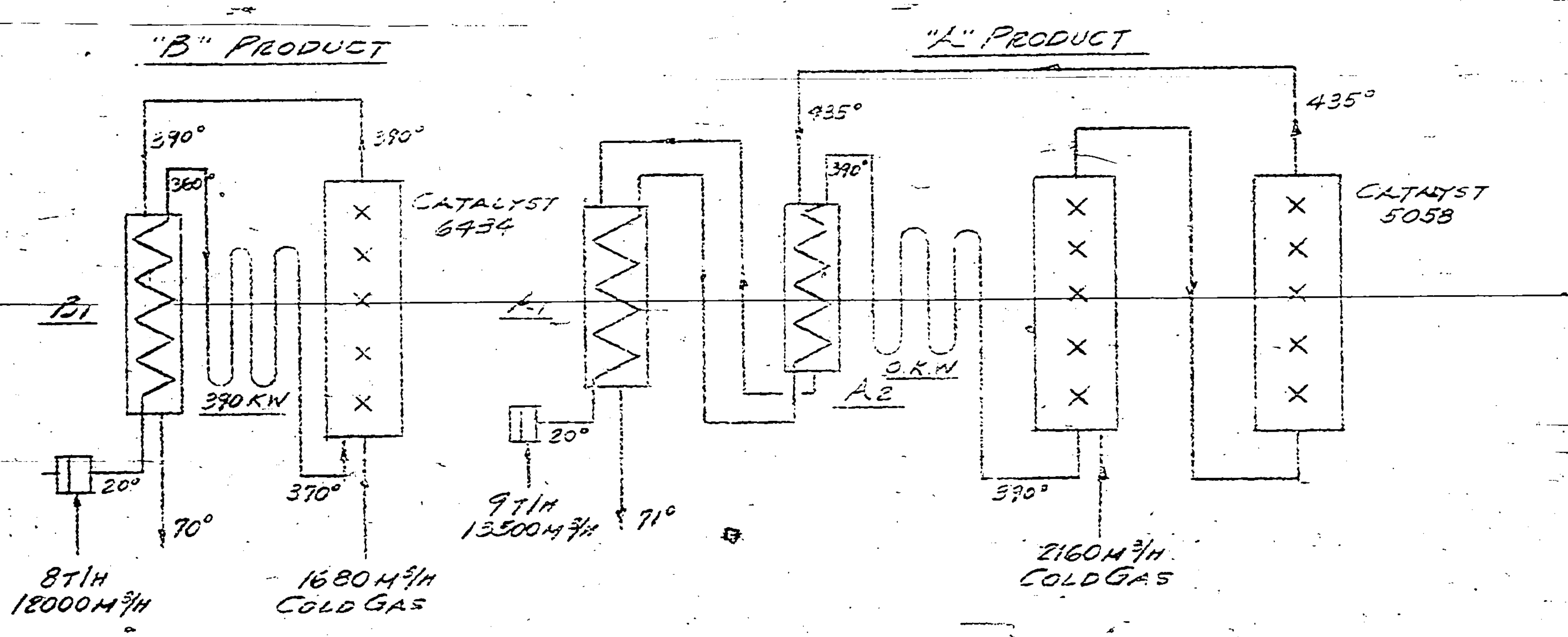
ARRANGEMENT 2



ARRANGEMENT 3



PRESENT ARRANGEMENT



TOM Reel 205,
Frames 733-737

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-199
KCBraun
12/27/46

The Influence of Temperature on the Results of Prehydrogenation (Saturation) with Concentrated and Diluted Catalysts. The Preparation of Such Catalysts.

Lu, 24. May 1943

In July 1941 systematic tests were made with the alumina-molybdenum-nickel catalyst 7846, the results of which are summarized in report 191051 of the 9. Aug. 1941, see the following pages. A test with 5058 is now under way. The stages of 20.5 MV(400°C) and 21.5 MV(417°C) have already been completed, i.e. a range in which an appreciable increase in splitting occurs (from 25 to 50%). A test with the alumina-tungsten-nickel catalyst 7846 W 250 = 8376 is planned.

Extract from Report 191051, of 9 Aug. 1941, on the Dependence on Temperature of the Hydrogenation Reaction of Scholven Bituminous Coal Liquifaction Middle Oil Over Catalyst 7846.

1). In the prehydrogenation of bituminous coal with catalyst 7846, usually done at 22.5 MV = 434° C, the temperature was varied between 7.5 MV = 175° C and 27.5 MV = 518° C and the results tabulated.

2). At 300° C = abt. 15 MV the catalyst begins to show hydrogenation effect as well as to reduce phenols and N-compounds.

3). At 23 MV = 442° C the maximum hydrogenation effect is obtained. The phenol reduction is already very good above 19.5 MV = 382° C, but the N-refining not below 21.5 MV = 417° C.

4). Practically no splitting of C-C combinations takes place below 22.5 MV = 434° C, gasification is correspondingly small. Splitting and gasification increase rapidly above 434° C. The formation of gasoline below 434° C is based primarily on phenol reduction.

5). Below 434° C the catalyst works fully reversible with respect to temperature changes. At temperatures around 500° C (aromatization range) the catalyst is damaged. However, it can be fully regenerated by burning in air and renewed sulfurization, so that it can again be used for prehydrogenation.

Preparation of 6434

A. - Composition:

The catalyst ready for filling consists of HF treated Terrana A extra and contains 10% WS_2.

B. Technical Preparation

1. Preparation of the mixture of hydroflouric acid treated Terrana and ammonium-sulfo-wolframate (Gelbsalz).

2. Decomposition of the amm-sulfo-wolframate for conversion into WS_2.

3. Preparation of the paste and its forming.

4. Drying of the shapes and their after-treatment.

300 kg. Terrana A extra from Südchemie, Deggendorf, Bavaria, are mixed with about 300-320 L of 8% HF-acid and stirred

in a closed, steam jacketed mixing vessel. After about 25-30 min. 500 L of a sulfur-ammonia solution of ammonium-sulfo-wolframate, containing 7% solid WO_3, are added. For the pre-preparation of the $(NH_4)_2WS_4$ solution, the mother liquor, obtained in filtering the $(NH_4)_2WS_4$ crystal paste in the preparation of $(NH_4)_2WS_4$, is used. It contains about 1-1½% insolubles as WO_3, 11-12% NH_3 and a total of 10% H_2S, and is strengthened with $(NH_4)_2WS_4$ to 7% WO_3. After adding the $(NH_4)_2WS_4$ solution to the Terrana, the live steam is turned on. The contents of the vessel, first fluid, then pasty, and finally granulated in the dry condition, requires about 8 hrs. for drying. The mixture of sulfur-ammonia vapor and steam escaping from the vessel during the boiling period goes to a closed absorption unit operated in closed circuit with the cooled sulfur-ammonia solution.

The dry product is sensitive to oxydation in the dry condition. The jacketed vessel containing the dry product is therefore water-cooled to room temperature before the product is removed. The dry product is gray in color.

To convert the $(NH_4)_2WS_4$ constituent into effective WS_2 the product from the mixing vessel must be heated to about 21-22 MV/408-425° C. For this purpose, the granulated product is first rough ground and then conveyed by means of spiral screws thru a system of closed horizontal ovens externally heated electrically. H_2 and H_2S is blown into the ovens at suitable points so that the decomposition of the $(NH_4)_2WS_4$ will takee place in a reducing atmosphere according to the following equation:

$$(NH_4)_2WS_4 + H_2 = WS_2 + (NH_4)_2S + H_2S.$$

The product from these ovens is continuously discharged thru a cooling space, collected in barrels protected from the light and then ground in a hammer mill to pass a 3 mm screen. The 6434 black powder so prepared is deep gray-black.

In order to form this powder into pills, it is first moistened by about 30 parts by weight of water. This is done in a vessel with built-in paddles. In moistening the powder the appearance of hydrogenation heat can be observed due to the absorption of water by the Terrana dried at 408-425° C. Since there is danger of oxydation of the finely distributed WS_2 in excessive heat, care must be taken that the powder is moistened in small batches of abt. 25-30 kg. and that the resulting paste is prevented from overheating by storing it in thin layers. Care must also be taken that only well cooled paste reaches the pill presses, otherwise the hydrogenation process, again released by the press heat, may cause the pills to heat up and oxydize the WS_2. The pills are then tumbled in a rotating screen drum to remove the burrs, followed by drying at abt. 7 MV/170° C, in which they shrink somewhat and harden. The drying is done in a vertical, externally electrically heated tube oven, thru which the pills are sluiced in a stream of N flushing gas. The dried pills are dove gray.

Finally, the pills receive an after-treatment in a similarly built oven @ 21-22 MV/408-425° C in a stream of H_2S flushing gas, to which a little H_2 has been added. The pills coming from this oven are screened and then represent the benzination catalyst ready for filling the converter. For cylindrical pills 10 mm dia. x 10 mm long the weight per liter = 0.90-0.92 kg. (The weight per pill = 1.24 grams and the compressive strength abt. 200 kg/cm²).

Adsorption of Hydrogen by Tungsten-Sulfide.

1. Preparation of WS_2

The WS_2 used for the adsorption tests was made from $(NH_4)_2WS_4$ by reduction with H_2 @ 350° C, carefully excluding O_2. The H_2 was freed of O_2 over platinum catalyst, cleaned with concentrated H_2SO_4 and dried. The reduction at the given temperature takes about 400 hrs. Even after this time small traces of H_2S appear. The reduction vessel is under a constant hydrogen pressure of abt. 150 mm Hg.

2. Adsorption @ abt. 25° C.

The adsorption increases appreciably up to 48 hrs. The final value is fairly constant up to pressures under 100 mm and equals abt. 1 cc H_2/g WS_2. At pressures below 100 mm the quantity adsorbed drops rapidly and equals only 0.45 c.c. H_2 @ 13 mm Hg, in a shorter test, to be sure.

Final Pressure	c.c. H_2/g WS_2	Observation Time.
466 mm	1.05	16 hrs.
211.6 mm	1.16	48 hrs.
109.5 "	0.96	16 hrs.
45.3 "	0.74	20 "
13.2 "	0.45	4 "

If only traces of outside air reach the catalyst its adsorption capacity drops sharply immediately to less than half. The values obtained with poisoned WS_2 are then very much scattered. The original activity could not be regained by renewed reduction with H_2 at the given temperature. It is still uncertain, whether this poisoning may be traced to O_2-absorption.

TOM Reel 188
Frames 20951-60

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-200

OPERATING BALANCE OF KOPPERS POWDERED COAL GENERATOR

Gasification test on Bituminous Coal Dust at Rheinpreussen Mine.

Analysis of dust

H_2O	1.95%	
Ash	8.75	Upper heating value 7977 h.u./kg
H_2	4.27	
Pure C	80.50	
Sulfur used	1.88	Lower heating value 7744 h.u./kg
N_2	1.19	
O_2	1.46	
	100.0	

Analysis of produced synthesis gases (test values)

CO_2	15. %	Upper heat value 2550 h.u./kg
CO	42.	
H_2	42.	Lower heat value 2347 " "
N_2	1.	
	100.0	

Gas yield (94% gasification)

$$\frac{(.805 \times .94)\ \frac{\text{kg C gasified}}{\text{kg coal}}}{\left(.57\ \frac{m^3/C}{m^3\ \text{gas}} \times .536\ \frac{\text{kg C}}{m^3 C}\right)} = \underline{2.47\ m^3/\text{kg dust}}$$

H_2 Balance

H_2 in product gas $2.47 \times .42\ \frac{m^3 H}{m^3 \text{gas}} = 1.038\ m^3/\text{kg dust}$

H_2 from feed powdered coal $0.427 \div 0.09 = .475$

H_2 from decomposed steam .563

Undecomposed steam at K = 2.34 at

1200° C. $2.34 \frac{\times .15 \times .42}{.42} \times 2.47 = .868$

Steam req'd	1.431
Steam from raw powdered coal 0.0195/0.81	.024
Actual req'd steam	1.407

Steam decomposition based on additional steam

	.563/1.431	39.3%

Steam decomposition based on H_2 content in gas produced .42/(.420 + .351) 54.3%

Oxygen Balance

O_2 in gas produced $(0.15 + \frac{.42}{2}) \times 2.47 = 0.890 \frac{m^3}{kg}$

~~O_2 from decomposed steam 0.563 ÷ 2 = 0.268~~

O

Additional O_2 required 0.622

Additional O_2 per unit synthesis gas

$0.622 \div 2.47 = 0.252 \frac{m^3}{m^3}$

Heat Balance

Input

Coal: 1 kg	Ho =	7977 h.u.	
Steam: 1.407 x 0.81 x 600		685 h.u.	steam used in process
1.407 x 0.422 x 1200		712 h.u.	excess steam
		9374 h.u.	

Output

2.47 m^3 synthesis gas x 2347 =	5800 h.u.
diff. Ho - Hu 2.47 x 203	510 h.u.
undecomposed steam	
0.868 x .81 x 600	422 h.u.
~~0.868 x .822 x 1200~~	~~439 h.u.~~
C-loss 0.06 x 0.805 x 8000	397 h.u.
Sensible heat in Product gas	
2.47 x 0.37 x 1200	1095 h.u.
Radiation + line loss	711
	9374 h.u.

~~711/7744 x 100 = 9.2 % loss on 1 kg powdered coal~~

Steam produced and used.
There is available for steam production:

$\underline{1095} + \underline{439}$ =	1534 h.u.
Waste heat loss:	
0.868 x 0.367 x 300 = 96	
2.470 x 0.330 x 300 = 244	
	340 h.u.
	1194 h.u.
Heat absorption in waste heat boiler:	
Steam production 1194 x .9 =	1075 h.u.
Steam consumption (1.05 kg at 3 ats)	-685 h.u.
Excess steam (0.52 kg at 16 ats, 350° C)	390 h.u.
Fuel required:	
Preheat 1.407 m^3 steam to 1200° C =	712 h.u.
Heat exchange loss (eff = 80%)	178 h.u.
Total fuel required	890 h.u./kg coal dust

Total Efficiency

$$\frac{5800 + 390}{7744 + 890} = 72.5\%$$

Gasification eff.

$$\frac{5800}{7744} = 75\%$$

Summary of Consumption + Production Figures

Quantity of powdered coal	1 kg
Synthesis gas produced	247 m^3
Upper heating value of gas produced	2347 h.u./m^3
Conc. of $CO + H_2$ in gas produced	84 %
Fuel per kg dust	890 h.u.
O_2 consumption 0.252 m^3/m^3 Sy. gas =	.622 m^3/kg dust
Excess steam production (16 ats, 350°) =	.52 kg
Inlet temperature (preheat) =	1200° C
Steam consumption covered by amm. prod (3 ats) =	1.05 kg
Outlet temp. of product gas after gasific.	1200° C

Gasification Test of Powdered Brown Coal from the Rheinpreussen Mine.

Analysis of the raw powdered coal:

Water	13.00%	
Ash	5.18%	
Pure C	56.20%	Upper Heat Value 5313 h.u.
H_2	4.71%	Lower " " 5120 h.u.
S by combustion	0.33%	
O + N	20.58%	

Analysis of gases produced: (80% concentration)

CO_2	19.0%	
CO	35.0%	Upper heat. val. 2430 h.u.
H_2	45.0%	Lower " " 2214 h.u.
N_2	1.0%	difference 216 h.u.

Amount of gas: 1.84 nm^3/kg raw powdered coal

C gasification:

$$\frac{1.84 \times 0.536 \times 0.54}{0.562} = 95\%$$

H_2 balance

H_2 in gas produced:	0.450	nm^3/nm^3
H_2 from raw powdered coal	0.284	nm^3/nm^3
H_2 from steam:	0.166	" "
Decomposed steam:	0.166	" "

O_2 balance:

O_2 in the gas 0.365 nm^3/nm^3

O_2 in raw coal: $\frac{0.20}{1.43 \times 1.84} = 0.076$

O_2 from steam: $\frac{0.166}{2} = 0.083$

0.159 nm^3

O_2 from outside sources 0.206 "/nm^3 synthesis gas

$0.206 \times 1.84 = 0.379$ nm^3/kg powdered coal

Steam Requirements:

Decomposed steam: $0.166 \times 1.84 = 0.304$ nm^3/kg raw coal

Undecomposed steam, k = 1.6 (1000° C)

$$1.6 \times \frac{0.19 \times 0.45}{0.35} \times 1.84 = 0.716 \text{ nm}^3\text{/kg raw coal}$$

Steam required 1.020 nm^3/kg raw powdered coal

Steam from moisture in combustible $\frac{0.13}{0.81} = 0.160$ nm^3/kg powd. coal.

Steam from outside x 600 = 0.860 " " " "

Decomposition of steam $\frac{0.304}{1.020} = 30\%$

Heat Balance

Brought in:

1 kg powdered raw coal u.h.v.	5313 h.u.	
steam: 0.86 x 0.81 x 600 =	417 " "	
0.86 x 0.422 x 1200 =	434 " "	
		6164 heat units.

Produced:

~~1.84 nm^3 sy. gas x 2214 =~~	~~4076~~ " "	
diff. upper and lower h.u.:		
1.84 x 216 =	397 " "	
undecomposed steam:		
0.716 x 0.81 x 600 =	348 " "	
0.716 x 0.41 x 100 =	293 " "	
Sensible heat of prod. gas:		
1.84 x 0.366 x 1000 =	225 " "	
Radiation and conduction loss =	151 " "	
		6164 h.u.

$\frac{151}{5120} \times 100 = 2.95\%$, referred to 1 kg raw powdered coal

Produced and consumed amounts of steam:

Available for steam production: 674 + 293	967 h.u.
Waste heat: 0.716 x 0.361 x 300 = 79 h.u.	
1.840 x 0.330 x 300 = 182 " "	
	261 " "
Taken up from heat boilers	706 " " 70 h.u.
Steam production: 3 atm $= \frac{706 \times 0.9}{651.2} = 0.97$ kg =	636 " " less
Steam consumption: 3 atm $= \frac{417}{651.2} = 0.64$	417 h.u.
Excess steam: 3 atm 0.33	219 " "

Fuel Requirements:

Preheating: 0.860 nm^3 steam to 1200° C	434 " "
Producer losses:(= 75%)	145 " "
Fuel to be supplied:	579 h.u./kg raw powdered coal

Total efficiency: $\frac{4076 + 219}{5120 + 579} =$ 75.5%

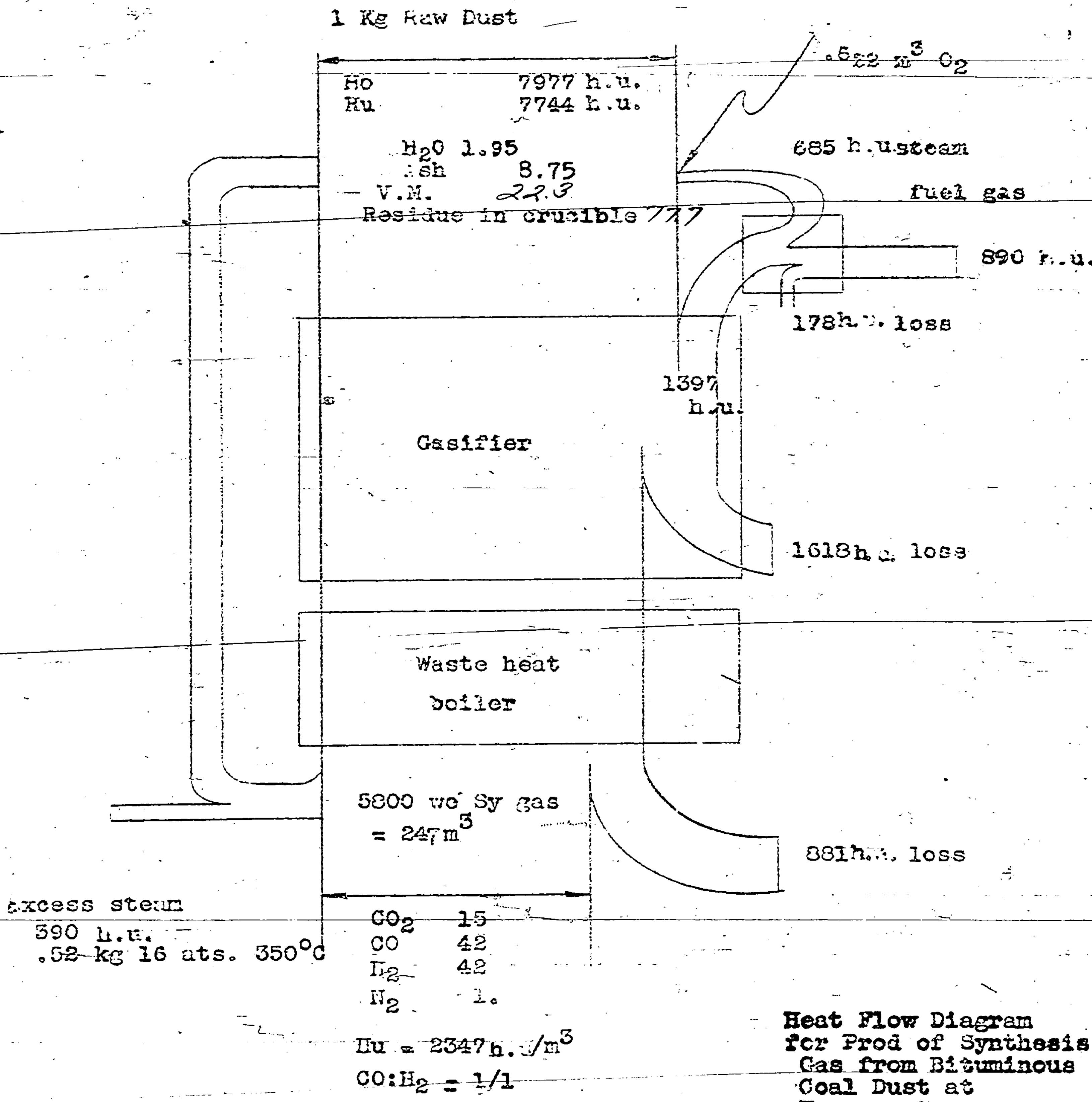
Gasification efficiency: $\frac{4076}{5120} =$ 79.6%

Summary of Consumption and Production figures:

Raw powdered coal:	1 kg.
Sy gas produced:	1.84 nm^3
lower h.v./nm^3 gas produced:	2214 h.u.
Concentration $CO + H_2$	80%
Fuel to be supplied per kg raw powdered coal	579 h.u.
O_2 consumption: 0.206 nm^3/nm^3 =	0.379 nm^3/kg raw powdered coal
Steam production, 3 atm	0.97 kg.
Steam consumption, 3 atm	0.64 kg
Excess steam, 3 at.	0.33 "
Intake temperature (preheating)	1200° C
Outlet temperature of the producer gas (v. heat flow sheet I.O.S. 178,467)	1000° C

/s/ for Heinrich Koppers, G.m.b.H.
illegible.

W.M. Sternberg
12/13/46



Heat Flow Diagram for Prod of Synthesis Gas from Bituminous Coal Dust at Koppers-Essen
6/17/43

TOM Reel 5
Pp. 307 & 315.

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-201

KCBraun
12/31/46

TYPICAL MONTHLY OPERATING REPORTS. GELSENBERG 1940 & 1941.

Index:

TABLE Ia -- DISTILLATION

ITEM	DISTILLATION B_1			DISTILLATION B_2			DISTILLATION $B_1 + B_2$
	t/h	S.G.	tons	t/h	S.G	tons	tons
Gasoline-Catchpot	21.07	0.7700	14899	21.05	0.7710	14881	29780
Return - run							
Thruput	21.07		14899	21.05		14881	29780
Raw Gasoline	9.89	0.7170	6988	9.70	0.7160	6853	13841
B-Middle Oil	10.39	0.8510	7353	10.07	0.8500	7126	14479
Offgas { B_1 = 207 600 $m^3 10^3$; B_2 = 322 300 $m^3 10^3$; 529 900	0.68	2.327	483	1.17	2.364	827	1310
Loss, { B_1 = 0.5% ; B_2 = 0.5%	0.11		75	0.11		75	150
Total	21.07		14899	21.05		14881	29780
Middle Oil Yield, %			49.3			47.9	48.6
Waste Water Total-417							

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TABLE I_b. STABILIZATION & WASHING

ITEM	STABILIZATION & WASHING C_1 t/h	S. G.	tons	STABILIZATION & WASHING C_2 t/h	S. G.	tons	$C_1 + C_2$ tons
Raw Gasoline	19.41	0.7170	13721				
Pure Gasoline	17.08	0.7315	12075				
Level Change in Vessels	-0.01		-6				
Offgas, 714.6 $m^3 10^3$	2.24	2.215	1583				
Loss, 0.5%	0.10		69				
Total	19.41		13721				
Pure Gasoline Yield, %			87.9				

TABLE I_c.--OPERATING DATA

PLANT	CONVERTER TEMPERATURES, °C Radiat. Zone (Bottom)	Radiat. Zone (Top)	Convect. Zone	OIL INLET °C	Atm. (Absol)	OIL OUTLET °C	Atm. (Absol)	FLUE GAS % CO_2	OPERATING HOURS
B_1	750	565	164	110	5.8	188	—	6.8	707.33
B_2	790	560	199	115	5.9	194	—	7.8	707
C_1									707

TABLE Id.--ENERGY DATA

PLANT	Electrical Energy	Fuel Gas	HP-Steam	LP-Steam tons		Sewer Water	Return Water	HP-Steam	Fuel Gas	LP-Steam Kg/t. Thruput	
	KWh x 10^3	$m^3 \times 10^3$	tons	Col.	Total	$m^3 \times 10^3$	$m^3 \times 10^3$	Kg/t. Thruput	m^3/t. Thruput	Col.	Total
B_1	51.0	606.6		226.3	269.3	27.7	489.5		40.75	15.2	18.05
B_2	51.0	670.5		237.2	270.3	33.0	263.0		45.05	15.9	18.2
C_1	47.0		812.8			10.8	49.5	59.2			
									HU (Kcal/m^3) 3244 3000		

TABLE IIa. A-DISTILLATION

	ITEM	A1			A2			A3			A4			Total
		t/h	S.G.	t	t/h	S.G.	t	t/h	S. G.	t	t/h	S.G.	t	tons
Incoming	Coal Catchpot	18.18	0.9700	13528	22.29	0.9690	16587	16.63	0.9710	12371	13.74	0.9670	10226	52712
Outgoing	Coal Gasoline	1.03	0.7333	766	1.14	0.7305	849	0.85	0.7358	621	0.76	0.7332	566	2802
	A-Middle Oil	8.59	0.9410	6389	9.90	0.9340	7366	7.99	0.9420	5942	6.46	0.9390	4803	24500
	Heavy Oil	8.45	1.0370	6290	11.12	1.0350	8271	7.73	1.0390	5754	6.47	1.0420	4813	25128
	Offgas,	0.07	2.1600	55	0.07	2.1150	50	0.05	1.8750	34	0.02	1.8450	14	153
	Offgas, m^3/h		34			32			24			11		
	Loss, 0.25%	0.04		28	0.03		51	0.03		20	0.03		30	129
	Total	18.18		13528	22.29		16587	16.63		12371	13.74		10226	52712
	M-Oil + Coal Gasoline Yield, %	52.9			49.5			53.1			52.5			51.8

Waste Water, 1321 m^3

Offgas, total $nm^3 = 75 \times 10^3$

Offgas, total $m^3/h = 101$

Offgas, mean density, $Kg/nm^3 = 2.04$

TABLE IIb. B-DISTILLATION

	ITEM	B2 - VT 707			B3- VT 707			B4- VT 707			B5 - CV 2b			Total t	Total t
		t/h	S.G.	t	t/h	S.G.	t	t/h	S.G.	t	t/h	S.G.	t	CV 2b	VT 707
Incoming	Gasol. Catchpot	8.74	0.7781	6500	32.22	0.7775	23969	15.39	0.7741	11447	18.46	0.8717	13731	13731	41916
Outgoing	Raw Gasoline	3.97	0.7195	2953	14.95	0.7191	11123	7.00	0.7152	5211	4.21	0.7823	3134	3134	19287
	B-Middle Oil	4.60	0.8400	3420	16.66	0.8396	12397	8.05	0.8389	5991	14.09	0.9884	10482	10482	21808
	Offgas	0.16	2.2530	116	0.56	2.1030	416	0.30	2.1580	225	0.08	2.0400	59	59	757
	Offgas, m^3/h		70			266			140			39			
	Loss, 0.22 %	0.01		11	0.05		33	0.04		20	0.08		56	56	64
	Total	8.74		6500	32.22		23969	15.39		11447	18.46		13731	13731	41916
M-Oil Yield, %		52.6			51.7			52.3			76.3			76.3	52.0

Waste Water, 447 m^3

Offgas, total $nm^3 = 383 \times 10^3$

Offgas, total $nm^3/h = 515$

Offgas, mean density, $Kg/nm^3 = 2.13$

TABLE IIc. — STABILIZATION & WASHING.

	ITEM	$C_1 + D_1$ CV2BL			$C_2 + D_2$ VT 707			Total
		t/h	S. G.	t	t/h	S.G.	t	tons
Incoming	Raw Gasoline & Liq. Petrol. Gas	4.56	0.7823	3393.0	29.26	0.7191	21773.0	25166.00
Outgoing	Pure Gasoline	4.29		3188.32	25.71		19130.19	22318.51
	Vessel Change	—		-3.00	—		-2.00	-5.00
	Offgas	0.16	2.0860	122.0	3.41	2.3290	2537.0	2659.00
	Offgas, m^3/h		79			1464		
	Loss, 0.77 %	0.11		85.68	0.14		107.81	193.49
	Total	4.56		3393.0	29.26		21773.0	25166.00
	Pure Gasoline Yield, %		93.9			88.0		88.7

Offgas, total nm^3 = 1148×10^3

Offgas, total nm^3/h = 1543

Offgas, mean density, Kg/nm^3 = 2.32

TABLE IId. OPERATING DATA

Plant		Operating Hours	Converter Temperature, °C Rad. Zone	Bridge	Outlet	Oil Inlet °C	Atm. (Absol.)	Oil Outlet °C	Atm. (Absol.)	Flue Gas % CO_2
	1	496.5	787	608	258	164	10.6	330	—	7
	2	734.0	728	561	222	153	8.3	315	—	—
A	3	536.5	755	525	218	155	10.6	310	—	6
	4	412.0	693	522	207	175	9.9	310	—	5
	1	—	—	—	—	—	—	—	—	—
	2	325.0	719	552	247	99	4.3	179	—	3
B	3	744.0	600	507	225	105	5.0	194	—	5
	4	419.0	552	468	228	112	4.2	189	—	5
	5	689.5	744	582	305	129	4.5	208	—	4
	1	291.0								
C	2	744.0								
	3									

TABLE IIe. ENERGY DATA.

Energy	Elec. Energy	Total Column Steam		HP-Steam	Fuel Gas	Fuel Gas	Sewer Water	Receiver Water
	MW	t	t	t	$10^3 nm^3$	10^6 Kcal (WE)	$10^3 m^3$	$10^3 m^3$
A 1	26.1	240	425	52	651	2344	11.8	96.5
2	39.2	276	489	60	851	3064	17.5	141.4
3	28.4	392	695	85	643	2315	12.8	103.0
4	21.7	284	506	62	518	1865	9.8	78.1
Total	115.4	1192	2115	259	2663	9588	51.3	419.0
Pr. t thruput x 10^3	2.2	22.6	40.1	4.9	50.5	182	1.0	7.9
B 1	—	—			—			
2	17.8	76	134	27	321	1155	13.2	60.6
3	41.0	293	517	104	999	3596	30.2	139.0
4	23.0	169	298	59	509	1832	17.0	78.2
5	38.1	189	335	69	619	2229	28.1	129.2
Total	119.9	727	1284	259	2448	8812	88.5	407.0
Pr. t thruput x 10^3	2.2	13.1	23.1	4.7	44.0	158	1.6	7.3
$C_1 + D_1$	5.4			598			7.1	48.5
$C_2 + D_2$	13.8			1552			18.0	124.0
$C_3 + D_3$								
Total	19.2			2150			25.1	172.5
Pr. t thruput x 10^3	0.8			85.6			1.0	6.9

UNITED STATES BUREAU OF MINES

CLASSIFIED LIST OF TRANSLATIONS BY THE COAL HYDROGENATION DEMONSTRATION PLANT, LOUISIANA, MISSOURI TO DECEMBER 31, 1946.

Arranged by W. M. Sternberg

THE FOLLOWING TRANSLATIONS ARE OMITTED FROM THIS CLASSIFIED LIST AND HAVE NOT BEEN REPRODUCED ON THIS REEL:

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T-19	T-108	T-119
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149.	Development of Liquid Phase Catalysts for Brown Coal.	75	638-639	
180.	Catalysts in the Production of Synthetic Fuels from Coal. By S. B. Tatarskii, K. K. Papok and E. G. Semenido. Neftanoie Khozyaistvo, vol. 24, #2, 1946.		52-55	
184.	Sulfidic Vapor Phase Catalysts, Especially Tungsten Sulfide in Industrial Coal Hydrogenation. Lecture by M. Pier, Ludwigshafen, 1943.	130	403-434	
185.	Operating Experience with Catalyst 7846-W-250 (8376) and a Comparison with 5058 and a Combination of the Two Catalysts. Stettin-Pölitz November 10, 1943.	130	460-483	

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