K 536

COMPOSITION: 60 p.b.wt. A.D.5 paste, 7.5 g HF / 100 g dry paste
40 " Terrana

5 g ZnO per 100 g carrier
2 g Cr from CrO_3 " " " "
10 g S as flowers of sulfur " " " "
0.8 g. Mo from $(NH_4)_2MoS_4$ " " " "

DATE OF PREPARATION: 1) 12/22/42 to 2/2/43
2) From April to end of May, 1944.

TOTAL PRODUCTION: 1) 9.091 kg = 14.8 m^3 10 mm rounded cylinders
2) 10,220 kg 16.6 m^3 " " " "

RAW MATERIALS:

1) A.D.5 paste from Süd-Chemie, Munich, shipment of 11/19/42; 60.0% H_2O

2) Terrana, extra, from Süd-Chemie, Munich, shipment 3/28/42

3) Hydrofluoric acid, techn. grade; from Dr. Reininghaus, Essen, 70-75%
HF by titration 72.6%; sp.gr. 1.13
Shipments of 12/2 and 12/23/42

4) Chromic anhydride, techn grade; Merck, Darmstadt, crystallized, 99%
CrO_3 by analysis 98.4%
Cr " " 51.6%
Used in 45 - 50% solution
From shipment of 11/10/42

5) Zinc oxide, technical grade; from Hamborn Zinkhütte, shipped 11/12/42

6) Sulfur, 95 - 100° from Dr. Reininghaus, Essen, shipped 12/9/42

7) Aqua ammonia, techn grade, from Overlach Bro's) M.-Gladbach
NH_3 contents from table 25.0%; Shipment of 9/8/42

8) Amonium sulfomolybdate, 98 - 99%; from Riedel E.de Haen, Hannover
The molybdenum content is always determined after receipt of a shipment, and solutions based on weight found. It varies between 30.0% to the theoretical value of 36.9%. When water content too high, 2%, water deducted.
Used in 20% solution of aqua ammonia, sp.gr. 0.910

COMPOUNDING: Charge — 65.0 kg dry material

Filling 90.0 kg A.D.5 paste 36.0 kg dry weight

added to it 4.1 " hydrofluoric acid
water depending on the consistency of the paste
8.0 kg terrana 8.0

	Kneaded for 30 minutes	
Added:	3.25 kg ZnO	3.25 kg dry weight
	5.00 kg H_2CrO_4 soln	2.50 " " "
	8.0 Terrana	8.00 " " "
	Kneaded for 10 minutes	
Added:	7.00 kg Aqua ammonia	
	Kneaded for 10 minutes	
Added:	6.50 kg flowers of sulfur	6.50 " " "
	Kneaded for 10 minutes	
Added	1.42 kg $(NH_4)_2MoS_4$ dissolved in	
	9.3 kg aqua ammonia	1.42 " " "
	10.0 kg terrana	10.00 " " "
		75.67 kg dry weight

Filling and emptying: 15 minutes
Total time per charge: 1-3/4 hours

STORING: The catalyst mass is pelleted immediately.

PELLETING: 10 mm rounded cylinders.

DRYING: 3 - 4 days at 60 - 70°

ACTIVATION:
Furnace: in boats, 500 - 600 li cap.
Gas rapid stream of H_2
Temp: 350°C --- 17.6 mv
Time: 8 hrs to bring up to temperature
4 " at temperature
10 " cooling

STORAGE: In 250 li Hauser containers.

USE: The hydrogenation division received on 2/23/43 the whole batch

DETERMINATION OF FILLING WEIGHT: -
Determined in container 23, using freshly prepared, still warm catalyst
volume of flask 265 li
filled with catalyst 162.5 kg
filling weight 61.5 te/m^3

Bottrop
21 March 1946

Ruhröl G.m.b.H

Catalyst in the stocks of Ruhröl G.m.b.h., Bottrop

	K 349	K 413	K 429	K 534	K 536
Stock	8.6 m^3	1.8 m^3	7.4 m^3	20.4 m^3	15.7 m^3
Within ovens of the stalls	-	-	-	15.7 m^3	15.4 m^3

Composition of the catalysts

% referred to carrier

	ZnO.	Cr.	S.	Mo.	Fe.	Pb.	
K 349	-	2.0	-	1.0	2.0	-	
K 413	5.0	2.0	-	0.4	-	-	
K 429	-	2.0	-	0.4	-	1.0	
K 534	5.0	2.0	5.0	0.7	-	-	
K 536	5.0	2.0	10.0	0.8	-	-	

Dr. Schirrmacher

/pkl

596 T-292

KCBraun
3-27-47

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

PROCESS FOR SPLITTING PRESSURE HYDROGENATION OF ASPHALTIC HEAVY OILS AND RESIDUES.

German Patent 727624
Class 12o, Group 105,
20. Feb., 1938

Issued To

I.A. Farbenindustrie A. G.
Frankfurt a. M.

By

Dr. Mathias Pier, Heidelberg, and
Dr. Ernst Donath, Mannheim.

DRP 727624

The production of middle oils, particularly diesel oils, from asphaltic heavy oils and residues of whatever origin by splitting pressure hydrogenation is difficult to accomplish in one operation, because the desired splitting takes place only above 450°C, at which temperatures, however, the asphalts present are separated and coked, so that the operation must be interrupted. For this reason the operation has herebefore been conducted in at least 2 stages, the first at temperatures below 450°C, preferably below 400°C, which reduced the asphalts, and the second at temperatures above 450°C, at which the splitting to middle oils was effected.

It has now been found that middle oils, particularly diesel oils, of the best quality can be obtained with good yield from asphaltic heavy oils and residues in one stage, without injuries by the asphalts present and with little gas formation and corresponding low H_2 consumption, if the feed materials are treated with H_2 at temperatures between 450 and 550°C in the presence of weakly hydrogenating catalysts at such a high thruput, above 0.5 kg, preferably 1 kg feed material per liter reaction space per hour and a pressure so far above 250 atm that the asphalt content, determined by the propane method, is reduced to less than 6%, preferably below 3%, and that 30 to 70%, preferably 35 to 60%, constituents boiling to 350°C, based on the liquid end product, are newly formed. The asphalt determined by the Holde method is reduced to less than 2%, properly below 1%, in this operation.

By weakly hydrogenating catalysts are meant those, whose effectiveness is below those of the sulfides of the metals of the iron group, known as hydrogenation catalysts. Under consideration are, e.g. porous substances, like Grude (lignite coke), active coal, iron oxide, fuller's earth, active silicic acid, kieselgur or magnesia, by themselves or together with small quantities of other substances, particularly oxides or other compounds of metals of the 5th and 6th groups, as well as iron sulfate, nickel sulfate or other sulfates.

The effectiveness of the catalysts is determined in the following manner:

A middle oil, boiling between 200 and 325°C, from mixed base petroleum, of a spec. gravity of 0.840, is passed over the catalyst, arranged in a fixed position in the reaction space, in vapor form, together with H_2, at a pressure of 200 atm and a temperature of 405°C, with a thruput of 1.5 kg oil per liter catalyst space per hour and an H_2 supply of 3 m^3 per kg oil. With the catalysts under consideration for this process less than 15 liters H_2 per liter reaction space per hour must be used. In general, 0.5 to 1 kg or more gasoline per liter reaction space per hour are formed herein.

Typical feed materials are heavy oils and residues containing about 6% to 65% asphalt, determined by the propane method, such as tars and crude oils, as well as liquid or meltable residues of pressure hydrogenation, splitting or extraction of coals, tars, mineral oils or similar substances.

To determine the asphalt by the propane method, the feed material is treated with 3 to 6 times the quantity of propane at about 60°C and a pressure slightly above the vapor pressure of the propane at this temperature. The asphalts are precipitated in this treatment. In the determination of the propane asphalt in the end product, it is advisable to drive off the lower boiling constituents by distillation and then determine the quantity of asphalt in the enriched residue.

The working conditions to be used for a certain feed material and catalyst are determined by pre-experiments, in which thruput, temperature and pressure are so adjusted that the above mentioned results are obtained, which will guarantee continuous operation as well as maximum yield, minimum gasification, best possible utilization of the reaction space and good quality middle oil.

The pre-experiments are conducted about as follows:

The feed material, e.g. the splitting residue of a crude oil, is subjected to splitting pressure hydrogenation in the presence of one of the above mentioned catalysts at a pressure slightly above 450°C and various pressures above 250 atm, e.g. 300, 500 and 700 atm, and with varying thruput, e.g. 0.7, 1.2 and 1.7 kg per liter reaction space. The investigation of the corresponding product of reaction obtained will then determine whether the prescribed results regarding asphalt content and the formation of middle oil can be achieved. If the conditions are met, the temperatures and thruput can be further increased, with generally better results. Pressure hydrogenation is then conducted under the conditions so determined.

The pressure range, determined in the above mentioned manner, for splitting residues of crude oils with various asphalt content can be taken from the following compilation. The pre-experiments to determine pressure and thruput for the feed materials to be used should be conducted within this pressure range.

Propane Asphalt	E_2-Pressure at a Temperature between 450 and 500°C
8 to 35%	300 to 500 atm
25 to 65%	400 to 800 atm

Depending upon the propane asphalt content of a feed material, the following pressures are derived:

Propane Asphalt	Pressure
8%	About 320 atm.
15%	About 360 atm.
33%	About 450 atm.
50%	About 550 atm.
60%	About 600 atm.

With many feed materials, it is further desirable, for determining the correct pressure, to take into consideration the amount of residue obtained in vacuum distillation at about 20 mm Hg. In general, feed materials with a residue of 10 to 25% are processed within a pressure range of 300 to 500 atm, and substances with a residue of 25 to 50% at pressures from 400 to 800 atm. Within the limits of the foregoing wide pressure ranges, the following pressures have been found satisfactory for various substances:

Vacuum Residue	Pressure
10%	320 atm.
15%	360 atm.
25%	450 atm.
35%	550 atm.
40%	600 atm.

If, e.g. the propane asphalt, as well as the quantity of vacuum residue, has been determined for a feed substance and it was found that, based on the above data, the pressures derived are comparatively far apart, it is advisable to conduct the pre-experiment at the mean pressure so derived, which will generally lead to success.

As already mentioned, thruputs of more than 0.5 kg, e.g. 1.2 to 1.8 kg or more per liter reaction space are used. In the processing of H_2-poor substances the lower limit of the given range is preferred and the upper limit for H_2-rich substances. It is further desirable to choose the thruputs and working temperature within the given limits so that more than about 200 m^3 H_2 per 1 m^3 reaction space per hour react with the feed substances.

With reference to the temperature to be used, it should be mentioned that it should not be so high as to cause troublesome dehydrogenation. The best way is to use a temperature so low that the spec. gravity of the fractions in the end product boiling above 325°C is not appreciably higher than in the feed substance, which is generally the case at temperatures between 450 and 520°C.

Example:

A splitting residue of an asphalt base crude oil containing 42% propane asphalt and 6% constituents boiling to 350°C, and which leaves 49% residue in vacuum distillation (at 20 mm Hg) to 325°C, is mixed with 1% Grude-coke soaked in a solution of iron sulfate, so that the Grude contains 10% iron sulfate.

The following operating method is determined by pre-experiments:

The splitting residue supplied with the catalyst, together with H_2, is preheated in a gas heated tubular preheater at a pressure of 600 atm and then conveyed thru an enlarged reaction vessel, with a thruput of 1.8 kg feed material per liter reaction space per hour. The product of reaction contains 57% constituents boiling to 350°C and 2.5% propane asphalt. Therefore 51% constituents boiling below 350°C have been newly formed. The gas formation is 10.6%, based on the constituents boiling below 350°C, including the gases formed. Constituents boiling to 350°C are returned to the reaction space after removing the catalyst, together with fresh feed material. In this manner, 17.5% gasoline and 71.5% diesel oil with a cetane number of 39 are obtained from the feed material. The total yield in hydrocarbons boiling below 350°C is, therefore, 89%. The H_2-consumption is 520 m^3 per ton of products boiling to 350°C.

If an operating pressure of 320 atm is used, with a thruput of 0.44 kg per liter reaction space per hour, a product containing 56% constituents boiling to 350°C is obtained. Gasification is then 16% and the propane asphalt content of the product of reaction 9.5%. The space-time yield is 0.22 kg of products boiling to 350°C per liter reaction space per hour, and the new formation of constituents boiling to 350°C is 50%. Besides, twice as much catalyst is required for continuous, trouble-free operation. The yield in gasoline and diesel oil is 84% when the constituents boiling above 350°C are recycled. The diesel oil has a cetane number of 32. The H_2-consumption is about 610 m^3 per ton of products boiling to 350°C. Compared with the operating method claimed herein the results of the comparative experiment are, therefore, considerably less favorable in every respect.

Patent Claim.

Process for the splitting pressure hydrogenation of asphaltic heavy oils and residues, characterized by treating the feed substances with H_2 at temperatures between 450 and 550°C in the presence of weakly hydrogenating catalysts with a thruput so high, above 0.5 kg feed substance per liter reaction space per hour, and a pressure so far above 250 atm, that the asphalt content is reduced to less than 6%, preferably less than 3%, and 30 to 70% constituents boiling to 350°C are newly formed.

C.H. — Patents

601 T-293

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3-27-47

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

PROCESS FOR CONTINUOUS LIQUEFACTION OF SOLID CARBONACEOUS SUBSTANCES

German Patent 722629
Class 12o, Group $1o_5$,
8. January, 1937

By

Shigeo Fujikawa, Dairen, Mandschukuo.

DRP 722629

In the known processes for the continuous liquefaction of solid carbonaceous substances by pressure hydrogenation it is customary to mix the powdered coal, etc. with a liquid medium, like tar oil or heavy oils, to form it into a doughy mass, to convey it under pressure into a reaction vessel and hydrogenate it. The use of oil makes it possible to inject the carbonaceous material into the reaction vessel by means of a high pressure pump. However, the heavy oils, etc. influence the conversion of the solid carbonaceous substance with hydrogen and may thus render liquefaction more difficult.

According to this invention, water is used to paste the finely powdered carbonaceous material, e.g. coal. The doughy mass so obtained is compressed by means of a high pressure pump and dried by circulating hydrogen under high pressure. It is then brought to the reaction temperature and conveyed to the reaction vessel provided with an agitator. Thus, we save heavy oil, etc. and the reaction between the carbonaceous substance and hydrogen is accelerated, because the material enters the reaction space in a dry state.

The feed materials for this process are solid fuels, such as brown coal or bituminous coal. Younger coals are particularly suitable, because they are most easily formed into a watery paste and are especially easy to liquefy.

It is known to drench or sprinkle carbonaceous substances to be subjected to pressure hydrogenation with a watery catalyst solution, then dry them and mix them into a paste with oils containing catalysts. Water, in this case, is, therefore, not used in the sense of the process at hand. In another known process, high pressure steam is used instead of high pressure hydrogen in the hydrogenation of coal. By comparison, in the process at hand the water is used to form a doughy mass from the finely powdered coal. Before hydrogenation, the water is again removed by the hydrogen circulating at high pressure.

The process is further described in the following example and attached drawing.

Example.

Powdered coal with 2% iron oxide as catalyst is mixed with an equal amount of water into a doughy mass in vessel 1. The mixture is compressed to between 2 and 50 atm in the low pressure pump 2 and to between 200 and 250 atm in the high pressure pump 3, and then conveyed to a drying autoclave heated to between 350 and 380°C. The doughy mass is here dried by hot hydrogen, conveyed in counter current to the doughy mass during its passage thru the autoclave with the aid of a conveying device. The mass is then conveyed to a preheating autoclave 5, where it is raised to between 380 and 400°C.

The high pressure hydrogen, which does the drying in the autoclave, is removed from the drying autoclave by means of a high pressure suction pump 9 and conveyed thru a cooling device 10, as well as a separating device 11, in which condensed water is separated. The water is drawn off from time to time thru a valve. The hydrogen, freed of water, is returned thru a heat exchanger 7 and a gas heater 12 to the preheating autoclave 5, from which it is conveyed to the drying autoclave 4. The hydrogen thus moves in a circulating system, consisting of the high pressure pump 9, heat exchanger 7, gas heater 12, preheating autoclave 5, drying autoclave 4, the cooling device 10, and the water separator 11.

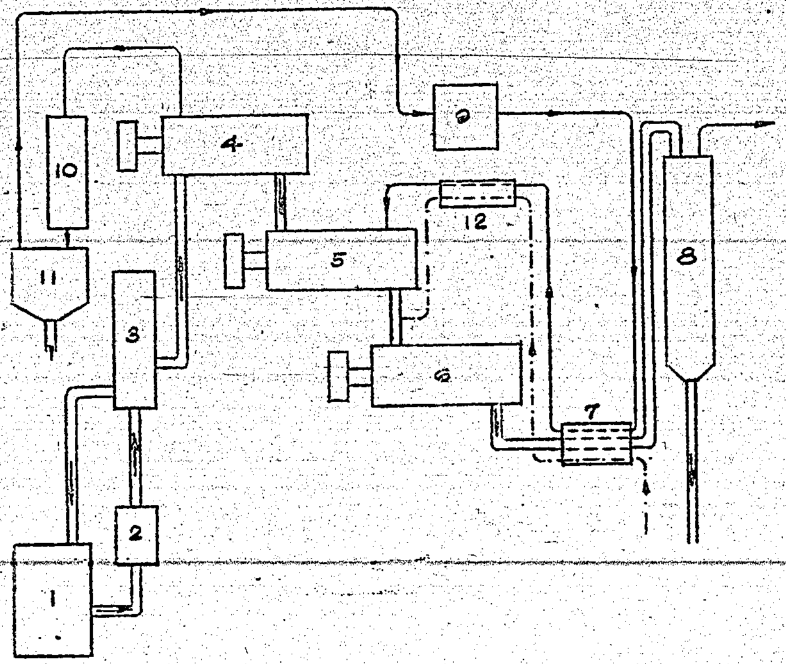
The preheated coal is taken in a dry condition from the bottom of the preheating autoclave 5 and enters a reaction vessel 6, provided with an agitator. Here it is brought into contact with preheated hydrogen, which, as shown in dotted lines in the drawing, has been conveyed thru heat exchanger 7 and gas heater 12 and heated to between 400 and 440°C, so that liquefaction in reaction vessel 6 can take place within a definite time.

The mixture of liquid oil and gas so obtained flows thru heat exchanger 7 and is drawn off from the high pressure oil separator 8.

In the processing of Fuschun coal, with a proportion between coke and volatile matter of 1:2, 0.4 to 0.7 kg coal per liter reaction space per hour could be liquefied in the described manner. In comparison with pasting the coal with oil, under otherwise equal conditions of reaction, a 30 to 40% greater liquefaction was obtained. The liquid oil obtained is a heavy fuel oil with a spec. gravity of about 0.9, which has the same properties as that produced by the known processes. The degree of liquefaction of the pure coal is about 90%. The heavy oil can be converted to gasoline by a second hydrogenation.

Patent Claim.

Process for the continuous liquefaction of solid carbonaceous substances, e.g. coal, by pressure hydrogenation and pasting with water, characterized by compressing the feed materials, pasted with water, by means of a high pressure pump, then drying them with hot circulating hydrogen under high pressure, heating them to the reaction temperature, and finally hydrogenating them in a reaction vessel.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C.H. Material Balances

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High Pressure Experiments,
Lu, 558

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

TWO PAPERS ON THE ACCURACY OF HIGH PRESSURE MATERIAL BALANCES IN TEN LITER CONVERTERS.

From Dr. Pier's files.

Jan. 8, 1942 Hu/Le

Summary

Some of the raw material balances obtained in the 5 liter converter operations 1197 for the production of middle oil and gasoline from coal did not agree as well as was desired. For this reason, the chance of errors of measurements affecting the raw material balance was investigated in hopes of finding means of raising the accuracy. At present, the scattering of the material balance values amounts to ± 2% which must be considered as satisfactory in view of the conditions of operation and the small amounts of materials used. The investigations disclosed essentially the following:

1). In most of the scattered results, irregularities were found in the weighing of the hourly production. These may be overcome, at least provisionally, by the use of collectors with vertical tubular sights.

2). The off-water, which excapes with the gas as moisture, may affect the raw material balance up to 1 %. This explains the variations in the almost always too low values for the water produced. The most effective means of checking it consists in an elementary balance, which must be performed as nearly as possible once in every series of experiments.

3). There exists up to 1% difference between the Podbielniak and vaporized gasoline high vacuum determinations, an explanation of which is being sought.

Study at the Different Accounting Centers.

The high pressure raw material balance in 10 liter converters is computed for the following subdivisions:

a) coal paste;	e) gas-containing and wet catch-pot
b) oil flushing	f) HOLD
c) Water injection	g) Off-water
d) H_2 consumption (calculated)	h) off-gas
total intake	total output

Notes, a) to c): Intake Accounting Posts.

The amounts of paste and flushing oil are estimated from the graduations on the suction container. The figures may in general be assumed to be correct. The occasional restandardization gave results in good agreement with the calculated values used previously, but irregularities have never the less been rather frequently observed, e.g. through sticking of the material to the mixer inside the paste storage tank, so that the calibration can not be sufficiently frequently controlled. Pump losses, resulting through bearing leaks are but infrequent; never the less that amount must be taken into account.

d) The consumption of hydrogen may be computed from the following average values, obtained previously in large scale coal hydrogenation:

	gH consumed/kg product
gasoline	90
middle oil	55
heavy oil	35
gaseous hydrocarbons	180

The consumptionscalculated in this way was compared with that obtained from material balance and was in rather good agreement with it. They were 3.3% too low on the average. The hydrogen consumption amounts to 2.7 - 3.2%, or 3% on the average, of the total intake (in grams) and the intake side of the raw material balance should be increased 0.1% on the average. The accuracy at these places is therefore entirely satisfactory. It remains yet to be determined from the voluminous available material to what extent the accounting bases would have to be changed in processes for an excess of heavy oil.

Outlet accounting posts: e - g):

The determination of the liquid products found by hourly weighings must be blamed for the most frequent uncertainties. Disregarding the fact that scales are frequently inaccurate because of the rather rough treatment, and require recalibration at regular intervals, losses during the filling and errors in handling are unfortunately not rare. Occasionally, when these errors amount to over ± 2% of the material balance, corrections are made on the strength of results from the preceeding days. The intended use of closed collector containers for the products with level indicators would produce a valuable improvement in the accuracy.

g) The proportion of off-water, which leaves in the form of moisture of the off-gases, is not at present taken into consideration. A comparison of the measured amounts of off-water with those which should be formed according to the elementary balance shows deficiencies of up to 137 g/hr. It must however be borne in mind that oxygen is determined by difference in the elementary balance, i.e. all the errors of analysis enter the values for oxygen, and may, of course, naturally become in part mutually compensated. The scattering of the off-water computations produced by them amounts, according to past experience, to ± 0.4% of the total raw material balance, This causes us to assume, that the calculated values for the off-water would increase the total materials balance to an amount of 1.0%. Presumably they are most affected by the temperature of expanded gases. This will readily explain the variations in the formation of fresh water expressed in percent to the pure coal, which also are scattered in the same proceedure by ±1.0. It must be mentioned here, however, that the nature of the preliminary treatment of the coal may affect considerably the new water formation through the additional oxidation of coal which has occasionally been observed and probably introduced during the grinding or drying.

h) The amount of off-gases (in g) is composed of the following:

1) vaporized gasoline
2) gaseous hydrocarbons
3) CO, CO_2, NH_3 and H_2S

The amount of vaporized gasoline in the off-gases is usually determined in a Podbielniak. A comparison with the high vacuum distillation method (Stockanalyse) shows the agreement to be rather poor. Were one to assume the results of the high vacuum analysis to be correct (and it probably is the more accurate method), one would find that in 5 cases out of 6 the Podbielniak analyses account for only one part of the vaporized gasoline, on the average about 50%. Podbielniak analysis indicates much less than the 60-70% vaporized gasoline actually present in the converter gas. This discrepancy, the significance of which has been underestimated in the past, may never-the-less reduce the amount of the total material balance by 1%. Dr. Meyer is now working on an explanation of the deviations.

In this connection, we investigated whether it was permissible to use 83.4% as the carbon content of the vaporized gasoline in the gasification. The vaporized gasoline from stall 1197 consists not only of pentane, but contains according to the high vacuum analysis results also around 15% C_6 hydrocarbons, and therefore 83.6% C. The agreement is entirely satisfactory, because with the assumption of 83.6% C the gasification would be changed by less than 0.1%.

The gaseous hydrocarbons were calculated in the balance from the C content of the hydrocarbons in the off-gases, after deducting the carbon in the vaporized gasoline, under the assumption of their containing on an average 79.0% C. The carbon content as determined from results of high vacuum analysis was 79.8%. The technical analysis frequently indicates somewhat less gaseous hydrocarbons, which however will affect the material balance so little, that it can be disregarded. The differences in the carbon gasified as hydrocarbons would have a considerable importance for gasification. On the average in the time interval here tested the values from high vacuum distillation were 5% higher (disregarding entrainment). This would represent a 0.9% increase in the gasification (referred to oil production + gasification)! In general, the gas densities computed from the industrial analysis are in better agreement with the determined densities, and are as a rule somewhat higher than the measured values, and the results of technical analysis may be used as a basis for the computation of gasification. The small content of gaseous hydrocarbons in the converter gases makes it very difficult to find a better analytical method.

An investigation of the sources of errors has shown, that the determinations of off-water, vaporized gasoline, and occasionally of the gaseous hydrocarbons are too low, but that when only around 98% of the proportion intake: output is found in the raw material, a correction in the catchpot and HOLD output is not necessarily indicated. A material balance which adds up to over 100% is, on the other hand, neccessarily burdened with larger errors.

All these sources of errors are usually kept within very narrow limits. Disregarding leaks, which can be readily corrected, one could estimate the uncertainties in the raw material balance to be around ± 2% in a 10 liter converter. This represents an accuracy which could not be improved with the small amounts of reacted substances.

The amounts of coal and oil are usually rather accurate in the material balance which means, that the uncorrected C balance are mostly very good.

/s/ Hüpfer

II.

May 18, 1942

THE ACCURACY OF THE UNCORRECTED ELEMENTARY BALANCE IN 10 LITER CONVERTERS.

In the tests with the 10 liter converters, the elementary balances are computed as material balances, i.e. they include the working-up of the residues. The low temperature carbonization gas off-water are estimated from the results of the laboratory tests with Fischer retorts, while distillation and centrifuging are estimated loss-free, because the losses there cannot be determined analytically.

The accuracy of 23 uncorrected elementary balances so far calculated have been tested. The little table below gives information on the average values, the scattering and the extreme values. Balances used in this test were based on evident errors, which could be readily corrected.

Balance	C	O	N	S
Average values, %	100.0	91.2	79.8	101.0
Average scattering, %	± 0.95	3.8	5.6	9.4
Extreme values, %	95.3-105.9	76.7-116.3	52.8-103.4	61.6-148.0

The carbon and sulfur balances add up therefore on the average to around 100%. Of the oxygen entering the reaction about 0.9% remains unrecorded, and escapes determination chiefly as moisture of the off-gases. About 20% of N is lost. It is assumed that it also leaves for the most part with the converter gas as NH_3. The primitive gas scrubbing on a 10 liter unit has not so far permitted any more accurate determinations.

The accuracy of the elementary balances (v. average scattering) drops in proportion to the amount present of an element in the total input from C to S, as could be expected.

On the average, the raw material balance (high pressure balance) add up to 99% with a scattering of ± 1.5%. No greater accuracy can be expected with a 10 liter converter.

/s/ Hüpfer, V. Hartmann

U. S. BUREAU OF MINES T-295
HYDRO. DEMON. PLANT. DIV.

EMERGENCY PRESSURE RELEASE IN HIGH PRESSURE STALLS

By Dr. E. Frese.

Whenever troubles occurs during operation of a high pressure stall, such as temperature rises, leaks in flange connections, valves, etc., the operating personel must immediately use rapid methods for correcting them. The proper treatment frequently determines whether the damage will be small, or will grow to major troubles.

It is therefore necessary to give some concrete directions to the converter operating personel, which would permit them to act quickly and independently in such emergencies. Asking for directions from the higher supervising personel requires time, and may cause damage, which could have been avoided, if the operating personel was properly instructed in the right procedure.

Every member of the operating personel has to perform certain definite tasks in case of an emergency pressure release, for the execution of which, and in their proper sequence, he is kept responsible. A frequent instruction of the personel in this service is important.

Precautions to be used in the liquid phase in case of trouble are different than in the vapor phase. As a general rule, temperature reactions proceed slower in the liquid phase, than in the vapor phase. They also frequently occur locally as reaction centers, which affect but little or not at all the adjoining thermocouples, or converter operation thermocouples. The most sensitive and dangerous parts of a stall are always the connecting pipe lines between the converters, which have a tendency to burst at high temperatures, and particular attention must always be paid to the last thermocouple of the converter. This last thermocouple in the liquid phase is frequently unaffected by the converter reactions, while in the vapor phase temperature rises in the converter always affect the adjoining couples and the outlet thermocouples.

The following preliminary directions are considered necessary for the converter operators at the Louisiana Plant:

1) Liquid Phase.

Similarly to the German installations, the converter temperatures will be 480 - 483° C. Should some converter thermocouple indicate 500 - 510°C, and it can no longer be cooled by increasing the cold gas flow, the coal paste must be completely or in part replaced with pasting oil, while the amount of injection is increased. The preheater temperature is to be simultaneously reduced. The converter outlet thermocouple is particularly to be watched for any temperature rises. These precautions are in most cases sufficient to prevent a rise, although some time will pass before they will begin to affect operations inside the converters.

Should the converter outlet thermocouple (the thermocouple of the connecting pipe line must be kept under observation) rise to 535°, or if some flange has sprung a leak in the stall equipment, or even a fire has started, one must proceed with the emergency pressure release. This is done as follows: a) The electrically operated intake and outlet valves must be closed (the stall separated from the circulation gas), and the make-up gas supply to the HOLD level indicator is turned off. The gas preheater is simultaneously put out. b) When these valves are closed (not before, since that would draw the vapor phase backwards) the let-down valves of the stall are opened up in the order converter II -> converter I and the pressure released by way of the needle valve in front of the pressure release tower. The pressure in the stall is simultaneously released as rapidly as possible to approximately 300 atmospheres by means of the pressure release valve on the suction side of the stall outlet, to leave the dangerous range of pressures. The pressure of all the liquid contents of the stall is released by means of the needle valve in the pressure release tower. The pipe line is briefly purged with hydrogen and next with nitrogen, and eventually with flushing oil. The residual gas pressure of the stall is released through the expansion valve at the stall outlet.

If the stall pressure would fall rapidly because of the bursting of some pipeline, or some other major leaks in the stall, efforts should be made to effect the let-down of the converters by a complete opening of the let-down valves and of the needle valve of the pressure release tower (eventually also opening of the by pass. The additional pressure release of the stall will in this case be omitted.

c) The hot and cold catch pots are to be let down in the usual way during the pressure release operations. All the gas inlet pipe lines (cold gas, HOLD level indicators, etc.) must be closed, to avoid any sucking in of the feed because of the differences of pressure.

d) The compressor operators for the make up hydrogen, the men servicing the gas circulation pumps, the feed pumps, the maintenance of circulation pressure difference, must be immediately informed of the steps taken, in most cases with direction to precautions to be taken in these departments (slowing down or complete shutting down.)

e) The paste pumps must be flushed with solid-free heavy oil after the pressure release, the let-down pipe lines of the converters and the hot catchpot must be purged with N_2. In the gas preheater, CO_2 is introduced with a closed outside vent in order to prevent the burning out of the tubes.

f) If the stall needs repair, it is flushed with N_2 to below 5% content of combustibles.

20. Vapor Phase.

The normal converter temperature is around 500° C. If a thermocouple indicates a temperature of 520°, and the temperature can not be reduced with cold gas, the amount of feed must be halved. Should the thermocouple reading reach 530°, the total injection must be stopped. In both cases, the combustion gas in the preheater must be greatly throttled. If a thermocouple reading should reach 540° the emergency pressure release must be begun.

a) The electrically operated gas intake and outlet valves are closed.

b) After they are closed, the pressure in the stall is released through the pressure release valve, in such a way, that the pressure drops from 700 to 300 atmospheres very rapidly (2 - 3 minutes) in order to leave the dangerous temperature region; the remainder of the excess pressure is reduced more slowly to protect the catalyst and the equipment, and in such a way, that in 8 minutes the pressure be reduced to 150 atm., after 13 minutes to 75 atm., after 18 minutes to 30 atm., and in 25 minutes to 0 atm. In particularly critical cases the pressure release must be accomplished still more rapidly, especially during the first moments.

c) The cold gas supply is cut off during the above operations, beginning with converter I.

d) The compressor operators for make up hydrogen, the service men at the gas circulation pumps and at the circulation pressure difference are to be immediately notified, informing them of the steps to be taken by them.

e) CO_2 introduced into the gas preheater.

f) Flushing with nitrogen in case of repairs.

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

PROCESS FOR PRODUCING GASEOUS HYDRO-CARBONS.

German Patent 725740
Class 12o, Group $1o_5$,
22. July, 1936

Issued To

I. A. Farbenindustrie A. G.
Frankfurt a. M.

By

Dr. Mathias Pier, Heidelberg, and
Dr. Hans Schmitt, Stettin-Politz.

DRP 725740

I has already been proposed to subject substances containing carbon to a pressure heat treatment under such conditions that more than 20% gaseous hydrocarbons are formed. The catalysts used in this process have been, e.g. oxides or sulfides of chromium, molybdenum or wolfram, either by themselves or on carriers, such as coke, active coal, quartz or active silicic acid.

It has now been discovered that in pressure heat treatment, particularly in pressure hydrogenation, of liquid carbonaceous substances, especially of hydrocarbons, under conditions forming large quantities of gas, e.g. 20 to 50% of the feed substances, a gas with a high content of hydrocarbons with more than one carbon atom in the molecule is obtained, if sulfides of heavy metals on fuller's earth (Bleicherde), previously treated with hydrogen-fluoride, is used as catalysts. It has been shown that it is possible to suppress the formation of methane in favor of such higher gaseous hydrocarbons by means of such catalysts. If the same heavy metal sulfides are used without a carrier, the formation of methane can be restricted only to a much lesser degree, by far.

Compared to the active coal already proposed as carrier for sulfides of metals for splitting liquid hydrocarbons to gaseous, the carriers according to this invention have the advantage of considerably greater mechanical strength, which is of particular importancefor the reactivation of the catalyst. Other known carriers, such as active silicic acid or fuller's earth not previously treated with hydrogen-fluoride, show a considerably lower effectiveness or a shorter effective life.

Particularly suitable feed materials are middle oils and gasolines, besides heavy oils. If solid feed materials, such as coals, peat or wood are used for producing gaseous hydrocarbons, they are first converted into liquid hydrocarbon mixtures. It is advisable to subject the feed materials to be processed, particularly those derived from coal or asphalt base oils, before use, to a refining process with liquefied gases, such as butane, propane, ethane, or chemical media, such as aluminum-chloride or sulfuric acid, or to refining pressure hydrogenation.

The pressure heat treatment of oils is done at a temperature between 400 and 700°C and a pressure of 20 to 200 atm, or more, properly in the presence of hydrogen. The choice of conditions is dependent upon the quantity of gas desired. The temperature is properly held about 20°C higher than in the usual pressure hydrogenation. While temperatures of about 400 to 430°C are used in usual pressure hydrogenation with sulfidic catalysts, for example, temperatures above 430°C are used in the process of this invention.

Another means of increasing the gas yield is decrease in thruput below the otherwise customary quantity, e.i. below about 0.5 kg, with H_2-poor feed materials, and below about 2 kg, with H_2-rich substances, per liter catalyst space per hour. The gas yield may also be increased by the return of low boiling products, such as gasoline, to the reaction vessel. These means can also be used together.

Example 1.

A petroleum middle oil at 480°C, together with H_2 at a pressure of 200 atm, is run over a catalyst produced by the deposition of wolfram-sulfide on Bavarian fuller's earth (Bleicherde), which has previously been treated with hydro-fluoric acid. 30% of the oils used are converted into gaseous hydrocarbons in this process.

The following table shows the composition of the hydrocarbon mixture so obtained and alongside of it the composition of a gas mixture obtained from the same oil under otherwise identical conditions but using the sulfide without a carrier, in %/wt., based on the gas mixture obtained.

	With Carrier	Without Carrier
CH_4	3	20
C_2H_6	2	22
C_3H_8	25	24
C_4H_{10}	52	20
C_5H_{12}	18	14

Example 2.

A middle oil from German petroleum at 450°C, together with H_2 under a pressure of 220 atm, is run over a catalyst produced by the deposition of wolfram-sulfide on fuller's earth previously treated with hydro-fluoric acid. With a thru-put of 0.7 kg. per liter catalyst space per hour, 32% of the feed material is converted into gaseous hydrocarbons of the following composition:

CH_4	0.7%
C_2H_6	0.8%
C_3H_8	14.0%
C_4H_{10}	84.5%

If active silicic acid is used as carrier, under otherwise equal conditions, the wolfram-sulfide is considerably less effective.

If a thruput of 1.5 kg at 420°C is used, so that only 6% of the feed material is converted to gaseous hydrocarbons, this gas has the following composition:

CH_4	17%
C_2H_6	12%
C_3H_8	27%
C_4H_{10}	44%

The example indicates that the formation of butane increases radically when working under conditions favoring strong gasification.

Patent Claim.

Process for the production of gaseous hydrocarbons with more than one carbon atom in the molecule from liquid, carbonaceous substances, particularly hydrocarbons, by catalytic pressure heat treatment in the presence of sulfides of heavy metals deposited on carrier substances, preferably in the presence of hydrogen, under such conditions that at least 20% or more of the feed material is converted into gaseous hydrocarbons, characterized by using fuller's earth previously treated with hydrogen-fluoride as carrier substance.

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3-31-47

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

PROCESS FOR THE PRESSURE HYDROGENATION OF COAL-OIL MIXTURES.

German Patent 725799
(Supplement to Patent 707851)
Class 12o, Group 105,
16, July, 1938

Issued To

I.A. Farbenindustrie A.G.
Frankfurt a. M.

By

Dipl. Ing. Hans Schappert, Ludwigshafen, Rhein.

DRP 725799

Patent 707851 concerns a process for the pressure hydrogenation of coal-oil mixtures, in which the greater portion of the mixture to be treated contains a smaller content of coal than the remaining smaller portion and is preheated by heat exchange with the products of reaction, while the mixture with the higher coal content is not preheated or only very little. The mixture obtained after combining both portions is preheated to the reaction temperature in a preheater. This operating method is intended to avoid the swelling caused by the preheating of coal-oil mixtures containing more than 50% coal, and which cause excessive wear in the preheater.

It has now been found that the heat exchangers can be protected from excessive wear by the same principle, if the feed-material, partly in the form of a coal-oil mixture with a comparatively low coal content and partly in the form of a coal-oil mixture with a high coal content, is preheated in such a manner that the larger portion of the material to be treated, with low-coal content, is preheated by heat exchange with the products of reaction, and the smaller portion, with high coal content, is preheated by outside heat sources, to or nearly to, the reaction temperature, whereupon the two portions are combined and conveyed to hydrogenation. The wear in the preheater caused by the mixture with high coal content can be readily prevented by wear-resistant material, because this preheater can be small in comparison with the heat exchangers for the greatest portion of the coal-oil mixture. This operating method prevents the cooling occassioned in the process of the main patent in mixing the portion with the lower coal content, preheated in the heat exchanger, so that a preheater for heating the mixture to the reaction temperature either becomes unnecessary or need be only very small.

The smaller portion of the coal-oil mixture with a coal content of 50 to 65%, for example is heated to approximately the desired reaction temperature in a gas-fired preheater provided with wear-resistant return bends, e.g. enamelled, and the larger portion of the coal-oil mixture, which may contain 42 to 45% coal, is heated to approximately the same temperature in a heat exchanger. The two partial streams so heated are then conveyed to the reaction vessel, either separately or combined.

As for the rest of the process, the conditions set forth in the main patent are valid.

The attached drawing illustrates the process in more detail.

The greater portion of the coal-oil mixture with the lower coal content, together with H_2, is forced from line "a" thru heat exchangers b and c by pump a, and thus brought to reaction temperature. It then flows directly into the first reaction converter e.

The two partial streams are mixed either shortly before or in the converter. The gas-coal-oil mixture now passes thru the reaction converters e, f and g connected in series. The sludge is separated in the catchpot h, from which it is drawn off thru line i, while the gas-vapor mixture escapes thru line k and gives up most of its heat in heat exchangers b and c to the coal-oil mixture with the lower coal content to be preheated. It is then cooled to about 40°C in the cooler l.

Patent Claim.

Change in the process according to Patent 707851 for the pressure hydrogenation of coal-oil mixtures, characterized by preheating the feed material, partly in the form of a coal-oil mixture with low coal content and partly in the form of a coal-oil mixture with comparatively high coal content, in such a manner that the greater portion of the material to be treated, with low coal content, is heated by heat exchange with the products of reaction, and the smaller portion of the mixture, with relatively high coal content, is heated by outside heat sources, to, or nearly to the reaction temperature, whereupon both portions are combined and conveyed to reaction.

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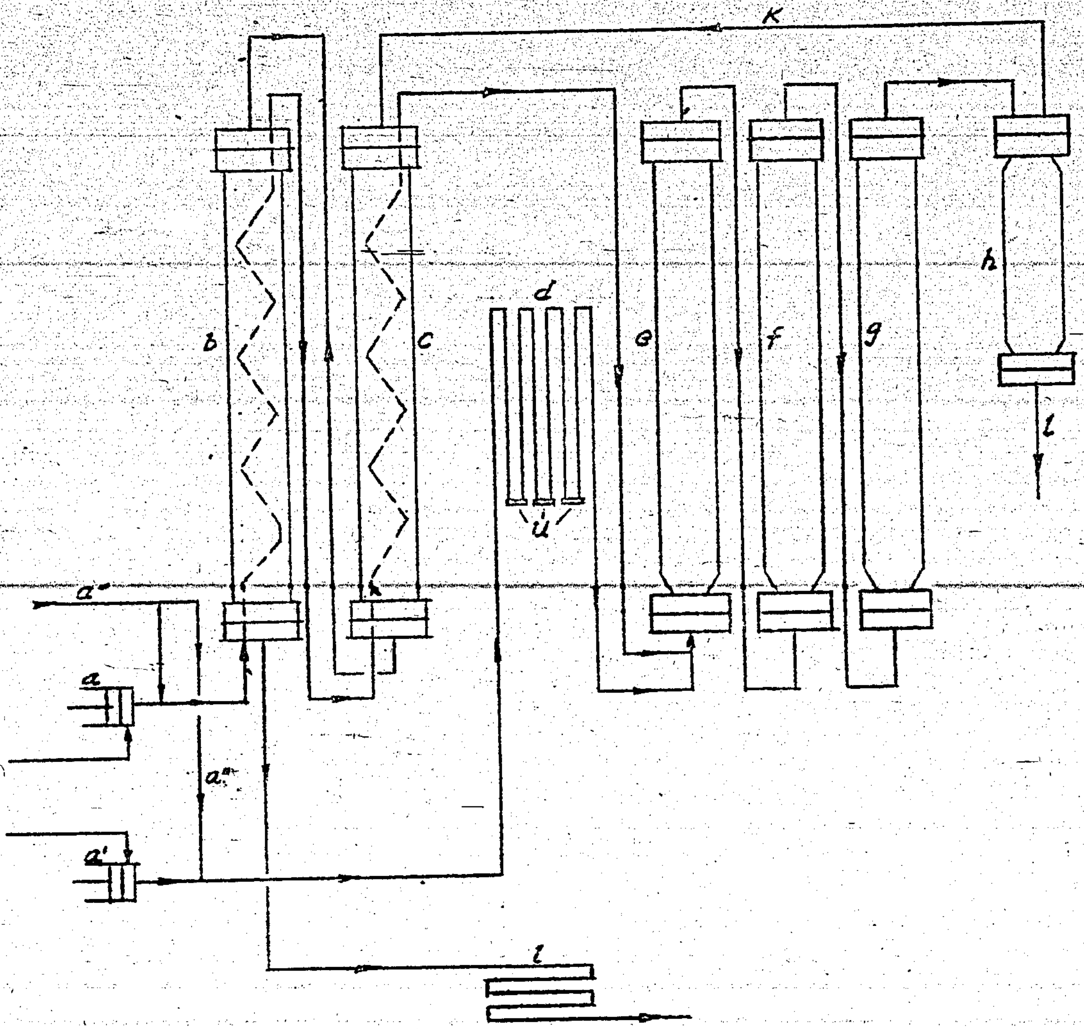

C.H. Rock Springs Coal

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

T-298

Dr. E. Donath
4/1/47

PRESUMED BEHAVIOR IN HYDROGENATION OF ROCK SPRINGS COAL

In the Report "Kohleanalyse Und Hydrierverhalten" (Coal analysis and behavior in hydrogenation) from Dr. Hupfer, Jan. 26, 1944, hydrogenation results in 10 l converters for various coals are compared.

The most important data from this report are given in Table 1. The connection of some analytical data with the carbon content of the maF coal may be seen in fig. 1. The variation of the hydrogenation results are shown in fig. 2. The relation between the carbon content and the other analytical data as well as the hydrogenation results is different for the coals from Upper Silesia and the Ruhr district. The coals from the Ruhr district contain for the same carbon content more net hydrogen and volatile matter and are easier to hydrogenate.

The analytical data for the Rock Springs coal coincide quite closely with the curves for the Ruhr coals. An extrapolation of the hydrogenation results with Ruhr coals to the carbon content of the Rock Springs coal gives the following specific data:

	Rock Springs Coal	For comparison Gelsenberg coal
% C in maF coal	79.7	83.9
Reaction temp. °C	469	469
% Coal conversion	96	96
Space time yield of Middle oil + gasoline kg/l.h	0.33	0.27
% Gas/MO + gasol. + gas	16	24
% Asphalt in pasting oil	6.5	8.5

To check these figures the ash analyses of Rock Springs coals should also be compared with those from Ruhr coals. The conversion figure is lower than that obtained at Pittsburgh in Operation 182, tests 4 and 5, viz. 98%. The reason for this difference is probably a low fusain content of the Rock Springs coal.

From the aforementioned specific data the following figures for the hydrogenation of Rock Springs coal are derived assuming two different losses in the HOLD recovery:

% C in HOLD - oil loss/maF coal	16	7
Middle oil + gasoline %/maF coal	62.8	69.3
% Hydrocarbon gases / " "	11.5	12.7
%CO / " "	1.7	1.9
$\%CO_2$/ " "	0.5	0.5
Thruput tons maF coal/m^3 h	0.53	0.48

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Table 1.

Coal origin	For comparison Rock Springs Coal	Upper Silesia							Ruhr			Saar		Lignites Rhe-nania	Centra Germa
T. G. Coal Nº		1262	1118	1263	1197	1180	1160	1174	1216	1090	1086	1060	1152	229	143
MAF Coal	0.521-0.536	0.554	0.553	0.578	0.565	0.577	0.588	0.587	0.560	0.568	0.609	0.572	0.558	0.458	0.40
% C	79.2-80.3	78.26	79.6	80.5	81.27	81.8	83.47	83.48	82.11	83.94	86.76	82.24	84.69	68.73	71.79
H	5.6-5.5	4.83	5.2	4.9	5.19	5.07	5.13	5.19	5.44	5.53	5.24	5.28	5.77	4.74	6.22
O	12.5-11.7	14.66	12.9	12.8	11.47	10.51	9.37	9.85	10.23	6.98	5.54	9.78	6.81	25.26	17.40
N	1.6- 1.7	1.82	1.5	1.5	1.94	2.31	1.66	1.03	1.26	2.30	1.83	1.46	1.85	1.19	1.33
S	1.1- 0.8	0.42	0.8	0.3	0.13	0.31	0.32	0.45	0.75	1.12	0.63	1.24	0.70	0.02	3.20
Net H/100gC	4.6- 4.5	3.3	4.0	3.7	4.1	4.0	4.3	4.4	4.7	4.9	4.7	4.5	5.3	1.9	4.9
% Tar	—	7.2	11.3	8.2	9.7	12.8	14.0	12.7	14.7	15.0	-	14.4	16.9	8.6	20.5
% Volatile matter	45.5 43.1	38.3	39.9	35.3	37.5	38.7	37.1	36.5	39.1	37.9	30.0	38.2	40.0	52.5	63.1
Wieluch Tridex x)															
Results in 10 L 700 atm Converter with Fe - catalyst															
Temp °C		471	470	468	471	474	472	470	(480?)	468	470	469	469	473	471
% Coal conversion		96.8	95.9	92.5	95.5	95.9	95.4	95.2	95.2	96.1	97.2	97.2	96.1	99.5	99.7
Space time yield - 325 °C kg/l.h		0.36	0.33	0.32	0.31	0.32	0.27	0.25	0.3	0.27	0.22	0.25	0.21	0.49	0.43
% C as gas/C in M.O. gasoline & gas		18.5	24.3	20	26.8	25.4	26.9	29.8	18.5	24.7	27.2	23.5	25.1	18.0	17.4
% Asphalt in recycle pasting oil		5.7	6.7	6.9	7.5	6.5	7.5	8.7	8.5	6.7	10.3	9.2	10.4	5.9	4.3

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x) Wieluch Tridex $= 1 - \frac{42\,H + 2.1\,O + 3\,N}{FC}$, where H, O, N and C are % on maF coal

Table 1.

Coal origin	For comparison Rock Springs Coal	Upper Silesia							Ruhr			Saar		Lignites	
														Rhenania	Centra Germau
T. G. Coal №		1262	1118	1263	1197	1180	1160	1174	1216	1090	1086	1060	1152	229	143
MAF Coal	0.521-0.536	0.554	0.553	0.578	0.565	0.577	0.588	0.587	0.560	0.568	0.609	0.572	0.568	0.458	0.40
% C	79.2-80.3	78.26	79.6	80.5	81.27	81.8	83.47	83.48	82.11	83.94	86.76	82.24	84.69	68.73	71.79
H	5.6-5.5	4.83	5.2	4.9	5.19	5.07	5.13	5.19	5.44	5.53	5.24	5.28	5.77	4.74	6.22
O	12.5-11.7	14.66	12.9	12.8	11.47	10.51	9.37	9.85	10.23	6.98	5.54	9.78	6.81	25.26	17.40
N	1.6- 1.7	1.82	1.5	1.5	1.94	2.31	1.66	1.03	1.26	2.30	1.83	1.46	1.65	1.19	1.33
S	1.1- 0.8	0.42	0.8	0.3	0.13	0.31	0.32	0.45	0.75	1.12	0.63	1.24	0.70	0.02	3.20
Net H/100gC	4.6- 4.5	3.3	4.0	3.7	4.1	4.0	4.3	4.4	4.7	4.9	4.7	4.5	5.3	1.9	4.9
% Tar	---	7.2	11.3	8.2	9.7	12.8	14.0	12.7	14.7	15.0	-	14.4	16.9	8.6	20.5
% Volatile matter	45.5 43.1	38.3	39.9	35.3	37.5	38.7	37.1	36.5	39.1	37.9	30.0	38.2	40.0	52.5	63.1
Wieluch Tridex x)															
Results in 10 L 700 atm Converter with Fe - catalyst															
Temp °C		471	470	468	471	474	472	470	(480?)	468	470	469	469	473	471
% Coal conversion		96.8	95.9	92.5	95.5	95.9	95.4	95.2	95.2	96.1	97.2	97.2	96.1	99.5	99.7
Space time yield - 325 °C kg/l.h		0.36	0.33	0.32	0.31	0.32	0.27	0.25	0.3	0.27	0.22	0.25	0.21	0.49	0.43
% C as gas/C in M.O. gasoline & gas		18.5	24.3	20	26.8	25.4	26.9	29.8	18.5	24.7	27.2	23.5	25.1	18.0	17.4
% Asphalt in recycle pasting oil		5.7	6.7	6.9	7.5	6.5	7.5	8.7	8.5	6.7	10.3	9.2	10.4	5.9	4.3

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x) Wieluch Tridex = $1 - \frac{42\ H + 2.1\ O + 3\ N}{FC}$, where H, O, N and C are % on maF coal

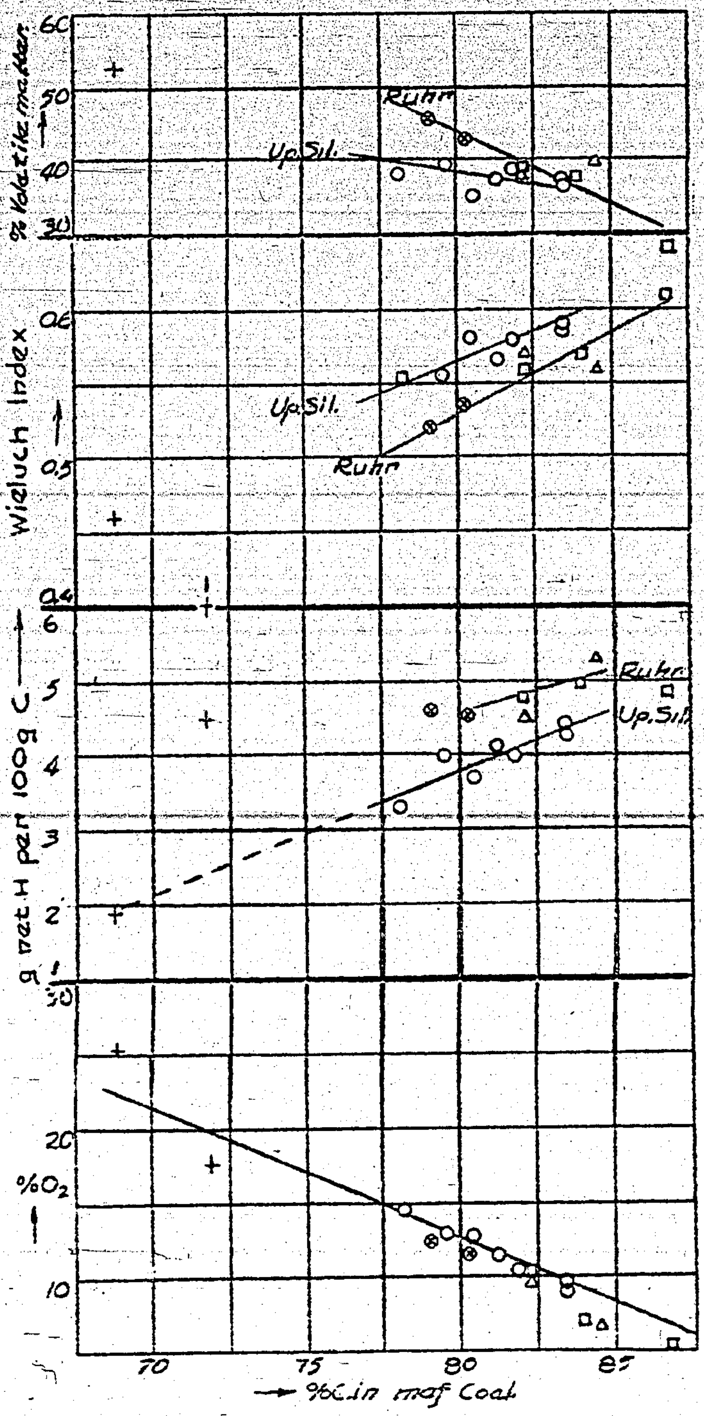


FIG. NO. 1.
Coal analysis and %C.
in maf. coal.

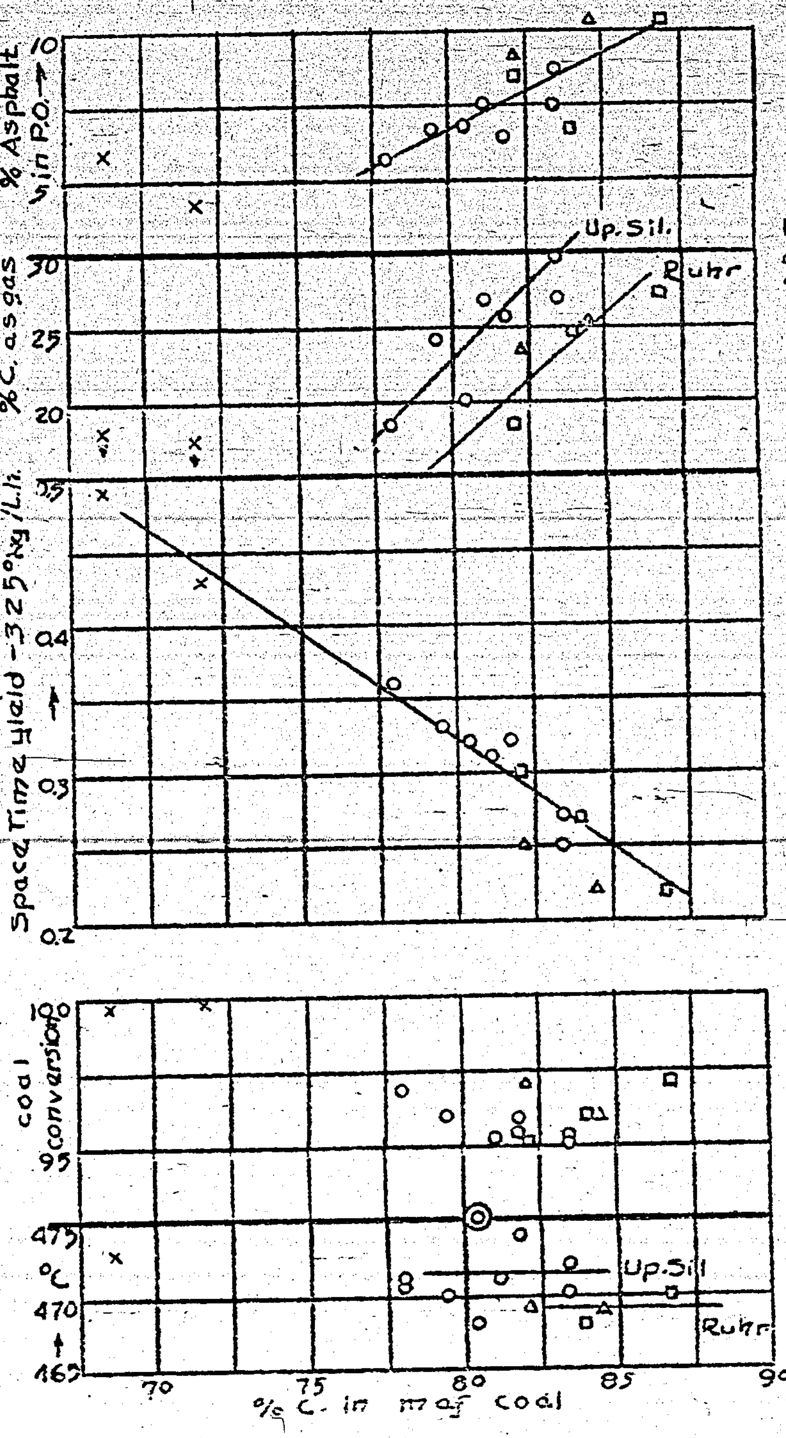


FIG. NO. 2.

L. Ph.-Hydrogenation results & % C. in maf coal.

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

T-299
W.M. Sternberg

TOM Reel 167,
frames 138 - 141

THE LIMITS OF SOLIDS AND ASPHALTS WITH LOW HYDROGEN SUPPLY IN THE LIQUID PHASE.

(Colloquium, Oct. 12, 1942)

The computation of the coal utilization and of the oil balance in the liquid phase is based on the determination of solids in hydrogenation products. The determination of solids may be done in a variety of solvents, which all give, as a rule, different values. The question therefore arises which solvents are best to use for the determination of solids.

Table I

Insolubles in	Benzol	Pyridine	Pyridine CS_2	Pasting-middle oil
HOID Gelsenberg	21.5	18.9	19.5	-
" Scholven	30.0	21.2	18.5	-
" extraction, Leuna, 700 atm.	9.8	-	-	6.9
Do, 300 atm.	21.3	-	-	11.8

The solvents selected must possess the following properties:

1) The solvent properties of the solvent must be as nearly the same as possible of the pasting oil in which the coal has been suspended or in which the hydrogenation residues of centrifuging or filtration will be worked up.

2) Under the conditions of analysis, the solvent must not dissolve any of the coal ingredients, or only very little of them.

3) The solvent must well dissolve asphalts and resins formed in the hydrogenation, and must under no conditions precipitate asphalts and resins, thus producing too high results.

All these conditions are naturally best satisfied by the same pasting oil as used in the operations. However, this oil can in most cases not be considered in the analysis because of its high boiling point. Solvents have accordingly been suggested for laboratory extraction, which approach in their properties the pasting oils as nearly as possible, but are readily volatile.

The solvent most frequently used is benzol.

An examination of Table I shows that the difference obtained with different solvents is very slight, when the hydrogenation conditions were good, e.g. in the process for the production of gasoline and middle oil at 700 atm, and one may well conclude, that benzol has very nearly the solvent properties of the pasting oil and extraction in it therefore represents correctly the degree of utilization.

Conditions are however completely altered when the hydrogenation conditions used were not satisfactory. E.g. in the process for the production of gasoline - middle oil at 300 atm., results obtained with different solvents vary a good deal, from which different utilization values would be deducted. Benzol gives relative high results with the Scholven HOID when compared with the better solvents for asphalt and the gums, such as pyridine. It is to be considered therefore, whether benzol does not indicate poorer values for the utilization, than one would obtain with the pasting oil used in the process.

When the hydrogenation conditions are still less favorable, such as during extraction under hydrogen, benzol, according to our results, must definitely not be used in the determination of solids. In this case, the return middle oil obtained in filtration or centrifuging of HOID is used as the pasting and thinning oil. The table shows that a much greater proportion of the HOID produced is soluble in middle oil than in benzol, and especially so in the 300 atm extraction, i.e. with the worst hydrogenation conditions. Were the utilization in this case computed from the results of the benzol extraction, a degree of utilization would be found which is much poorer than one would find in actual working up of the residue by filtration or centrifuging.

This leads to the conclusion that substances, which are precipitated by benzol, are formed under poor hydrogenation conditions. When the hydrogenation conditions are good, such substances do not form, or else they form at the start, and are so changed by subsequent hydrogenation, that they lose their insolubility in benzol.

We have a few determination of insolubles in the case of extraction from Upper Silesian coal at 300 atm of hydrogen which permit drawing some deductions on the properties of these substances insoluble in benzol.

Table II gives the ultimate analysis of some benzol and middle oil insolubles.

Table II.

	Benzol insolubles	Middle oil insolubles	Substance soluble in middle oil and insoluble in benzol (calculated)
% C	88.73	91.29	86.30
% H	3.70	3.77	3.63
% O	4.26	1.26	7.12
% N	1.52	1.59	1.45
% S, volatile	1.79	2.09	1.50

The substance soluble in middle oil and insoluble in benzol shows a surprisingly high percentage of oxygen. A decomposition of asphalts made according to Suida and Motz gave the following results:

24.1% hard asphalt and carbenes
23.8% asphalt resins
35.6% oil resins
16.0% oil

These middle oil soluble and benzol insoluble substances are therefore principally resins.

Bitumens appearing in certain extraction processes contain these resins in greater or smaller amounts. We understand under bitumens in this connection the filtrate from the extraction process freed from middle oil. These bitumens are soluble in middle oil, and must be considered as hydrogenation products.

The analysis of different bitumens is shown in Table III, where they were broken down with benzol and petroleum ether, and also some breaking down by the method of Suida and Motz-Lemme into hard asphalt, asphalt resins, oil resins and oil.

The products are so arranged in the table, that the hydrogenation conditions have been improved from left to right. Welheim operates at 100-150 atm in the absence of gaseous hydrocarbons merely in the presence of middle oils, which give up hydrogen. In the Ludwigshafen extraction tests at 300 atm of hydrogen, the hydrogenation and splitting conditions are better than in Welheim, while at pressures of 500 and 700 atm this is true to an even higher degree.

Table III.

Nature of the bitumen	Welheim bitumen	Lu 300 atm bitumen extraction	Lu 500 atm bitumen extraction	Lu 700 atm bitumen extraction
% insol. in benzol (benzol solids)	62.0	28.5	21.2	9.2
% insol. in benzol soluble in gasoline (s-asphalt)	18.4	24.1	24.8	26.0
% soluble in benzol and gasoline (oil)	19.6	47.4	54.0	64.8
% hard asphalt and carbenes	60.5	26.1	13.9	7.2
% asphalt resin	5.5	11.1	3.0	6.1
% oil resin	23.0	26.3	34.0	67.2
% oil	10.5	36.5	49.2	19.5

The benzol - gasoline breaking down, as well as by the Suida-Motz-Lemme method, show a relationship between the components of asphalt and the hydrogenation conditions. In the least hydrogenated and split Welheim bitumen there are 62% bensol insolubles, in the 700 atm hydrogenation only 9%. The s-asphalt increases somewhat with greater hydrogenation.

Much hard asphalt has been found by the Suida and Motz-Lemme method, which decreases steadily with greater hydrogenation, while the asphalt resins exhibit hardly any change.

The characterization of the bitumens, as well as of the hydrogenation conditions can very well be done by the Suida and Motz-Lemme, as well as by the method of solubility in benzol and gasoline. The example shown gives information that a comparison of determination of solids by extraction in pasting oil (e.g. liquid phase middle oil) with the benzol extraction method could be used as an indication of good or poor hydrogenation conditions.

It may very well be that benzol-insoluble oil constituents are formed during hydrogenation from an incomplete or deficient hydrogenation.

The high and low temperature coking offers a parallel to the coal hydrogenation. The high temperature tars, and the hydrogenation products obtained from them, also contain benzol insoluble substances, and so do the L.T.C. tars from bituminous coal. E.g., in the flushing gas tars, the so-called red resins are insoluble in benzol. These resins are to a great extent decomposed by cracking in the hot surface low temperature carbonization. We have learned that these resins consist to a great extent of unsaturated hydrocarbons, which are unstable and very sensitive to temperatures. One naturally gets the idea that the resins precipitated by benzol in both the hydrogenation and in the L.T.C. are principally decomposition products of the bitumens, and that they only become soluble in benzol by additional hydrogenation or cracking.

/s/ Rank.

/fkp

U. S. BUREAU OF MINES T-300
HYDRO. DEMON. PLANT DIV. W.M. Sternberg

11/11/42

EXPERIMENTS ON MIXING OF COAL PASTE

From Dr. E. Frese's files.

An abstract

Two kinds of coal paste are required if heat exchange is used for coal paste in hydrogenation plants, the thick paste and the thin paste, the solids content of which must be kept at a certain maximum for efficient operations of the heat exchanger and preheater. Variations in the solids contents observed at the paste pumps of the Stettin coal hydrogenation plant, which was the first to use heat exchangers, were traced to the poor results obtained with the mixing orifice and the stirrer in the supply tank, because our preliminary experiments have shown that there is no settling of a homogeneous thin coal paste in the pipe lines even when heated to the operating temperatures. From a practical standpoint, a sufficient improvement of the mixing of the thin paste is produced by replacing the mixing nozzle with power stirrer which guarantees a sufficiently uniform mixing of the components, and permits using the supply tank with a stirrer merely as buffer tank. On the strength of qualitative and quantitative tests with a laboratory model, a suitable mixer for a continuous production of thin paste is recommended, with the production of 1.14 te/hr, and which consists of a 10 vane double turbine with a pipe line and breaker arms. The mixing action is increased by such location of the feed line that the mixture of thick paste and oil, entering at the bottom will be just sucked out, and will remain as long as possible in the pump for better mixing. The relationships existing between the laboratory model and the industrial size unit are used in the determination of the rpm, mixer dimensions, recirculation and power requirements to produce geometrically similar flow conditions in the laboratory and industrial models. Experiments in the laboratory model and theoretical considerations of stirring and mixing processes have resulted in producing useful suggestions for the improvement of the thin coal paste preparation in Stettin.

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

KCBraun
4-2-47

FILTRATION OF COAL EXTRACT AT WELHEIM

By Rank & Orth, Ludwigshafen
25 February 1942

(Report of a visit to Welheim)
(See also T-177 and T-206)

The experimental filter put at our disposal is a column filter (Kerzen) consisting of 12 columns with a total filter surface of 8.2m^2. The capacity of the filter housing is 2.7 m^3. The construction of the filter is illustrated in attached Figures A and B.

Welheim has recently made some fundamental improvements on the filter cake discharge device. The shut-off gate valve formerly used has been replaced by a mushroom closure (cone) held against the sharp edged seat by nitrogen pressure. It is intended to replace the nitrogen by oil pressure to avoid trouble by nitrogen failure. The lift of the cone is 220 mm.

The discharged cake drops thru the opened closure into a container under inert gas (CO_2) pressure, from which it is discharged into a Redler conveyor thru a chute by a revolving rake. The Redler conveyor is also under CO_2 pressure. The Redler conveyor is protected against wear by reinforcing plates. The conveyor delivers the filter residue thru a distributor into two (2) Büttner L.T.C. kilns. The filter residue contains about 30% oil, the kiln residue recovered from it about 0.3% oil and 30% ash. The kiln residue goes to the boiler house for fuel.

The column (filter) material is a quartz refractory, furnished by Schumacher, Bietigheim. Welheim has tried out several pore sizes, BRG50,-40, -30 and Ultra. At the present time, BRG 40 is in use. It has 36% pore surface and will pass 100 liters of water in 100 seconds at 1 atm absolute pressure. By comparison, the Ultra material will pass 100 liters in 200 seconds, which means a 50% decrease in capacity. Welheim is satisfied with the purity of the BRG 40 filtrate. Leaks in the filter columns hardly ever occur at Welheim, although the tension spring must be drawn as tight as possible in assembly. The seals between the rings (Klingerit) are dipped in water glass before assembly. Experience at Welheim has shown that the wire reinforcement on the filter column rings cannot be dispensed with, because they will crack too easily, otherwise. In new columns the wire is wrapped spirally over the entire length of the column. Experiments with columns of longer elements, 5 to 6 cemented rings, are also planned.

The life of the columns is 1000-1500 filtrations, wherein four (4) tons of raw feed per filter unit of 22 m^2 filter surface is processed per filtration. An average of three (3) filtrations per hour are made, which

/

corresponds to a filter capacity of about 500 kg. of raw feed per m^2 filter surface per hour. The used filter elements have not been successfully regenerated, so far, and are thrown away. The dismantled columns show only very little deposit of residue between the wire rings. Filtration is done to a cake thickness of 1.5 to 2 cm, the smallest distance between the cake layers is then about 6 cm.

The raw feed is filtered undiluted and contains about 10% residue coal and 24% bitumen. The filtration temperature is 140 to 160°C. The hot material is discharged from high pressure into raw feed containers provided with agitators and heating coils to supply the heat lost in radiation. The gas off-takes from the raw feed containers communicate with the gas off-takes from the pure filtrate containers. Raw feed, as well as wash solvent, are recirculated to prevent settling. The raw feed is conveyed by Atlas steam pumps of a capacity of about 200 m^3/h and the wash oil by multi-stage centrifugal pumps. The filter units are connected to the circulating lines as shown in Figure C.

Three filter units of 32 columns and 22 m^2 filter surface each are available. The filtration pressure is 4 atm. The filters operate with an overflow limited by an orifice (Blende). The filtration time proper is from 3 to 6 minutes with a total operating time of 17 to 20 minutes, depending upon the age of the columns. The wash filtrate is returned to high pressure as pasting oil. The filter cake is expelled with CO_2 @ 7.5 to 8 atm. This pressure may be lowered if the cake is expelled with a sudden shock. A rapid-opening valve is used for this. The bricks (filter elements) are flushed during refilling of raw feed by applying CO_2 pressure from the inside to the outside. Filling and emptying times are kept as low as possible to keep up the capacity and prevent damage to the filter by drying out. The filling time should be about 2 minutes. When the filter is shut down it is filled with middle oil. The valves are operated by hand wheels, for which ~~2 men per filter are required. The CO_2 consumption is 700 m^3/h/filter unit.~~ Welheim is short on CO_2 and is considering cleaning and recycling of the used CO_2.

The two (2) Büttner kilns for deoiling the filter residue have a capacity of 1.5 t/h and do not operate very satisfactorily because of leaks inherent in the construction. Welheim proposes to replace them by another type.

The topping of the pure filtrate is done in two (2) stages. In the first stage it is concentrated to 50% bitumen content, in the second to 100% bitumen @ 220°C softening point. Discontinuous vacuum agitation is used for this. The preheating is done in horizontal gas heated pipe coils. Continuous operation (short column) has recently been adopted, though the second stage is still in the experimental stage. Holding the level in the column is waived herein. The bitumen is granulated in a water trough and drained on a vibrating screen. A small water content of the granulate does no harm, because the electrode coke is made by adding steam anyway.

In cooperation with a filter manufacturer, presumably Imperial, Welheim is developing a continuous pressure filter. Dr. Schmitz rejects the use of a "filter aid", or filtering agent, because of the difficulty of its equal distribution on the columns and for economic reasons.

/pkl

EXPERIMENTAL COLUMN FILTERS WILHEIM

T-301

FIG. A FILTER CONSTRUCTION

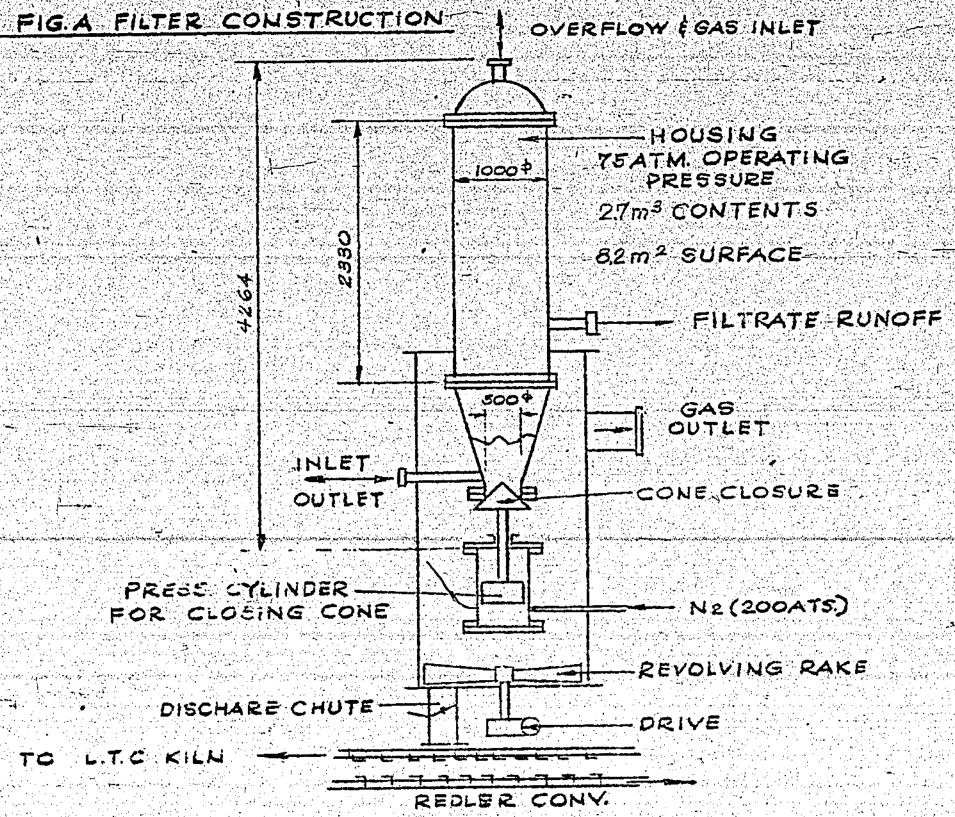


FIG. B SECTION THRU HOUSING

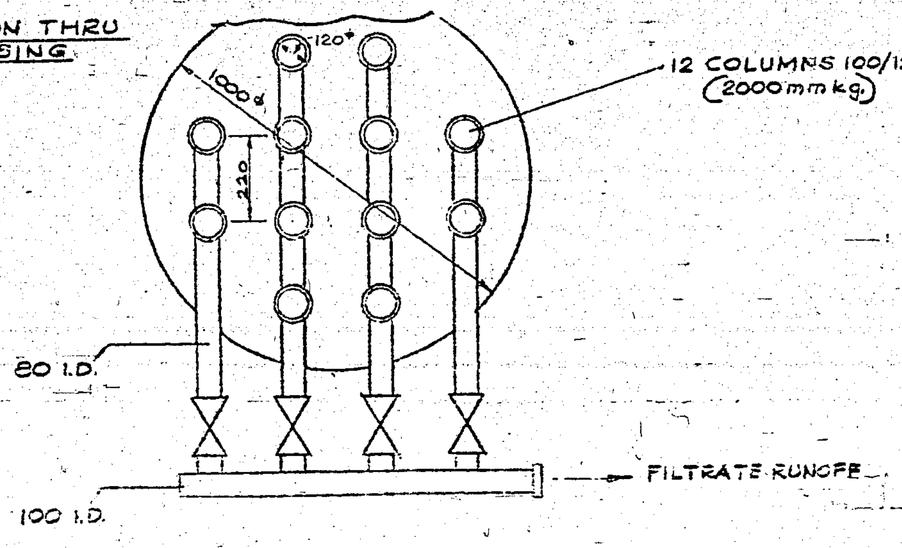
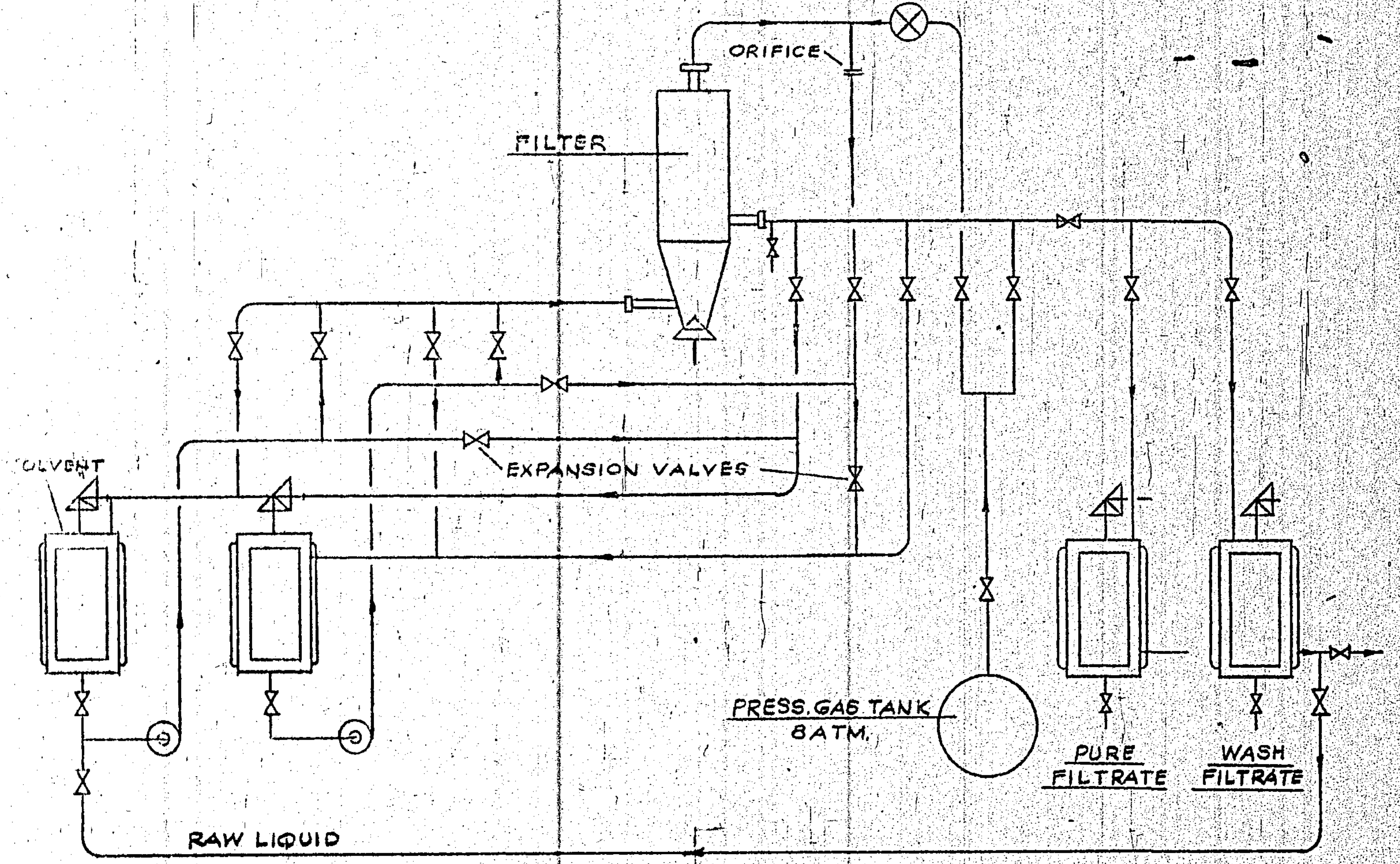


FIG. C

GENERAL ARRANGEMENT OF FILTER EQUIPMENT



C.H. Cat.

Dr Storch

634 T-302

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

Remarks on Liquid Phase Catalysts

By Dr. E. Donath, April 2, 1947

Introduction

In the vapor phase testing of catalysts small converters with about 50 ccm catalyst volume give quite reliable results. This is mainly due to the following facts:

the experimental difficulties are small;

the reaction in the vapor phase is nearly pure catalytic, the influence of thermal reactions being negligible;

presuming good temperature control only the space time yield of gasoline and the gas formation must be determined.

Of course, the decrease of catalyst activity and quality of gasoline have also to be evaluated, but this can be done in separate experiments and only with a small number of selected catalysts.

In the liquid phase, however, the amount of thermal reactions is considerable, therefore the influence of catalysts on the reaction more difficult to determine. In addition the coal hydrogenation reaction is influenced to a considerable extent by the quality of the recycled pasting oil and the amount of settling of catalyst and solids and of stirring in the converter. Furthermore the asphalt and solids content, the coal conversion and the composition of the new formed oil must be determined besides the space time yield of new formed oil and the tar formation. That means that autoclave experiments fail to give a complete picture of the performance of a liquid phase catalyst. Experiments in continuously working converters must be made and the influence of the recycled pasting oil and trouble freeness of operation observed.

Vapor phase catalysts have an influence on the following reactions: removal of oxygen, sulphur and nitrogen, hydrogenation of olefinic double bonds and aromatic rings, severance of carbon to carbon bonds. Each of these reactions can easily be studied in model experiments. For the coal hydrogenation model experiments are more difficult. Therefore, conclusions as to the action of the liquid phase coal hydrogenation catalyst are difficult, because they are made usually from a very complex reaction. The splitting and hydrogenating action of a very active catalyst, viz chlorine, in small scale experiments may be seen from the following table:

Catalyst	0.06% Tin Oxalate	0.75% Chlorine + 0.06% Tin Oxalate
Coal conversion	1.0	1.0
M.O. Space Time Yield	1.0	1.2
Gas Formation/M.O.	1.0	0.9
Asphalt content of pasting oil	1.0	0.8

It may be remarked that the slowest reactions in the liquid phase bituminous coal hydrogenation seems to be the conversion of asphalts to oil and the conversion of heavy to middle oil.

Abridgement of the development of liquid phase catalysts.

For the hydrogenation of lignite tars in liquid phase initially finely ground molybdic acid in a concentration of 20-30% was used as a very active catalyst. The total HOLD with the catalyst was recirculated and an almost complete conversion to middle oil obtained. Also for lignite molybdic acid (soaking with ammonium molybdate solutions) as catalyst gave good results. It came in commercial application when it was found that only an amount of 0.02 - 0.05% on lignite is necessary if 25-50% of the alkalinity of the coal ash is neutralized with sulfuric acid.

As it was found impossible to recover the molybdenum at reasonable costs from the hydrogenation residues, other catalysts were studied. Finally, satisfying results were obtained with about 5% iron oxide on lignite, omitting the neutralization with sulfuric acid.

In the liquid phase hydrogenation of tar and oil residues, the activity of the recirculated molydbic acid was impaired by small amounts of inorganic and organic solids. Therefore, here the use of high catalyst concentrations was abandoned and only small amounts of catalyst were used and discarded together with a small amount of HOLD, containing also the inorganic and organic solids and resistant asphalts from the feed. To obtain the optimum effect and avoid the settling out of the molybdic acid, this was used on support. The best and cheapest carrier was steam activated lignite semi-coke (grude), soaked with sulfuric acid in order to neutralize 90% of the alkalinity of the ash and with 2% of molybdic acid as $(NH_4)_2MoO_4$. This catalyst was comercially used. It was replaced only because of the scarcity of molybdenum in Germany by a grude catalyst containing iron sulphate and sodium hydroxide. This catalyst was not as active as that containing molybdenum, but its activity was high enough to maintain a trouble free operation of the commercial plants without a sensible reduction in thruput.

For the hydrogenation of bituminous coals also, molybdenum oxide (coal soaked with ammonium molybdate) was used with good results as catalyst. Later it was found by the I.C.I. that hydrochloric acid (also hydroiodic acid) is a very active catalyst for the bituminous coal hydrogenation. It is favorably used together with tin. Usually 0.06% tin oxalate and 0.75% chlorine as ammonium chloride were used, however the high corrosivity of hydrochloric acid, especially at the temperature of water condensation, necessitates a neutralization of the hydrogenated product before the heat exchangers. Tin and chlorine catalysts were used commercially at the Scholven plant. The tin oxalate was later on replaced by a tin ore residue containing about 15% tin. The same results with this material were obtained, using the same amount in terms of tin.

At 300 atm pressure good results were obtained with bituminous coals of a carbon content not exceeding about 83%. For higher carbon content coals, a sufficient asphalt hydrogenation was obtained at 600 atm hydrogen partial pressure. At this pressure, however, the chlorine corrosion was worse. Therefore, catalysts were tried which should permit to work without chlorine and which also are available in Germany.

Considering the successful use of iron catalysts for the lignite hydrogenation, similar catalysts for the bituminous coal hydrogenation were tested preferentially. It was found that finely divided iron oxide obtained by soaking the coal with $FeSO_4$-solutions worked satisfactorily at 700 atm pressure. 1-1.5% of this catalyst was sufficient if in addition 1.5% of iron oxide (e.g. Bayermass) were used. An addition of sodium sulphide seemed to give improvements with coals of low sulphur content. It was, of course, necessary to neutralize the chlorine content of coals when this was high enough to cause corrosion. The performance of iron catalysts in commercial plants was tolerably satisfactory as far as the hydrogenation reaction itself is concerned, however these catalysts caused some trouble by scale formation especially in the preheater.

Liquid phase catalysts for the Louisiana plant.

Considering the low carbon content of the Rock Springs coal and the pressure of 700 atm, there seems to be no need to use chlorine as catalyst. Of course, with chlorine as additional catalyst to tin or molybdenum, higher thruputs and yields are attainable. The following catalysts, employed in commercial or semi-commercial equipment, may be considered for the Louisiana plant, omitting all catalysts used only in small scale experiments:

Iron catalysts	(1.2% $FeSO_4$·FMoO, 1.5% Bayermass*)
Tin	(about 0.06% tin oxalate)
Molybdenum	(about 0.02-0.05% MoO_3 as $(NH_4)_2MoO_4$ solution)

These 3 catalysts should be compared under similar operating conditions in small scale experiments. For the tin and molybdenum catalysts, an alkaline reaction should be avoided by adding ammonium chloride, but to prevent chlorine corrosion, the chlorine content of the undiluted liquor must be kept below 0.04 at most 0.1 g** per liter. If the natural chlorine content of the coal is too high, corrosion can be avoided by adding an amount of sodium sulphide to the coal sufficient to keep the chlorine content in the liquor below the mentioned limit.

If the results with tin or molybdenum as catalysts were comparable to those with the iron catalysts, the former are to be preferred because there is less danger of scaling and only a small amount of solids is introduced. The experiments with these catalysts would give reliable results if they were made under reaction conditions as similar as possible to those expected in Louisiana. That means that the new formed oil consists of middle oil and gasoline besides the heavy oil loss. The HOLD recovery should also be similar to that in Louisiana in order to obtain a similar recycle pasting oil.

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* Inasmuch as the Rock Springs coal contains sufficient sulphur, no addition of Na_2S will be necessary

**If in this case the liquor or the layer between the oil and liquor contain black flocks of FeS, the chlorine content is too high.

If this is not possible, an indication of the relative activity of the catalysts could be obtained in autoclave experiments. Experiments in continuously working converters at the same conditions and with the same pasting oil would give more reliable results comparing the asphalt reduction and product yields and space time yields with different catalysts.

/fkp

Carbonization

DR. STORCH
T-303

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

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KCBraun
4-2-47

INCREASING THE YIELD IN LOW TEMPERATURE CARBONIZATION

(See also T-110)

A. By Adding Thinning Oil to Catchpot.

By Hupfer & Leonhardt
Ludwigshafen, 21 April 1943

Experiments in Scholven have shown that the injection of thinning oil (catchpot heavy oil) into the hot catchpot changes the letdown composition so that the asphalt content is approximately 1/3 lower than that calculated with the thinning oil included (See Scholven reports of May 9th and December 16th, 1942). If the letdown is diluted only after it has left the catchpot, as is done in normal centrifuging, such a lowering of the asphalt content does not occur, according to the Scholven method of splitting A + B + C asphalts. Scholven explains the influence of the injection of thinning oil into the hot catchpot on the asphalt content in this manner, that components of the letdown are still held in solution, which otherwise flocculate in the undiluted letdown in the catchpot and are thereby changed so that they cannot be dissolved later.

In consequence of the reduction of asphalt in the letdown, Scholven observed an improvement in the L.T.C. yield from 65 to 73%, based on the oil in the letdown.

The Scholven results were tested in an experiment with K 1242 (Beuthen-Heinitz), which was run to gasoline plus middle oil in a 10 liter converter with iron-sulfate, Bayermass and ammonium-chloride @ 600 atm. and 470°C.

In this test, the addition of thinning oil (catchpot heavy oil) to the catchpot was made in two (2) different ways. It was injected into the pressure equalizer of the catchpot once, and into the neutralizing vessel connected to the catchpot the other time.

The quantity of the thinning oil was proportioned so that a letdown with about 16% solids was obtained, i.e. the proportion of the letdown oil to catchpot heavy oil was the same as the normal in the centrifuge residue. The letdowns obtained were analyzed for solids and asphalt content, as usual, and were further carbonized (L.T.C.) in the Fischer retort. As a check similar tests were made on a normal letdown and are diluted to 17% solids. The results are tabulated below:

Letdown	Th. oil inj. to neutral. vessel	Th. oil inj. to press. equal	Diluted normal letdown	Normal Letdown
Bensol-Solids, %	14.2	17.8	17.0	20.3
Ash in whole, %	8.5	9.3	8.7	8.5
S-asphalt in whole, %	6.3	6.4	7.3	8.5
S-asphalt: ash	0.74	0.69	0.84	0.84
L.T.C. yield of oil in L.T.C. feed	83.1	82.5	82.0	77.1

The effect of a reduction in s-asphalt by the addition of thinning oil to the hot letdown under pressure was, therefore, verified, even though the asphalt reduction (about 17%) was not as great as in Scholven. By comparison, only a slight improvement in the L.T.C. yield was observed, which might be still within the range of possible errors.

Experiments in the Laboratory and in the Plant to increase the Yield in L.T.C. Oil in Low Temperature Carbonization of Asphaltic Residues.

By Dr. Horn & Dr. Hinz
Stettin-Politz
14 December 1942

In the low temperature carbonization @ 530°C in the ball kiln a loss of 10 to 15% is generally suffered with pitch letdown and one of 20 to 30% with centrifuge residue from Silesian coal; the losses based on the oil obtained free of water and solids. The reason for the following experiments was the fact that various materials, added to the feed for other reasons, reduced the yield in L.T.C. products. This phenomenon led to the idea that the yield could probably also be increased by the addition of suitable substances, which either decreased the always observed additional coking of a part of the injected oil or decreased gasification.

Pitch letdown, obtained in the hydrogenation of bituminous coal tar pitch, was used first as feed material for the experiments, later centrifuge residue obtained in centrifuging coal hydrogenation letdown.

A. - Experiments with Pitch Letdown.

The work was taken up in our laboratory so that pitch letdown, also processed in the plant at the time, was carbonized in the Fischer L.T.C. retort. This material, with the addition of superheated steam, produced the following yield balance in the laboratory: 72.5% oil, 3.8% gasification, 23.7% additional coking.

To increase the yield, we started with alkali and earth alkali hydroxide catalysts and could clearly observe that the yield was reduced thereby, as e.g:

with $Ca(OH)_2$: 65.2% oil, 5.8% gasification, 29.0% coking,
" NaOH : 60.2% " 3.6% " 36.2% "

It was also found that oxides of copper, molybdenum, uranium, wolfram, chromium, nickel, and others, cause no effect. The same thing was observed in the L.T.C. of centrifuge residue with the given additions. Metals like copper, chromium, aluminum and alloys, of which Raney-Nickel seemed especially suitable, were out of place here.

Based on the idea that perhaps more oil is formed by the polymerization of the light constituents or that this might be obtained by dehydrogenation, and splitting of high asphatic molecules, experiments were started with sulfur, selenium and tellurium, since these substances are frequently used as catalysts for the reactions just mentioned. A small increase in the yield in L.T.C. oil from pitch letdown was obtained, 2 to 2.5% with tellurium, 1 to 2% with selenium (red), and 0.5 to 1% with sulfur. Obviously, it could be maintained that such differences are within the range of possible errors, inasmuch as it was found that the yield was higher in the plant than in the laboratory, 72.5% oil in the laboratory against 83-88% in the plant. This difference may be explained by the fact that our materials were heated in the laboratory to 520°C at the rate of 5°C per minute and then carbonized in 1/4 hour, while in the plant the material reaches its final temperature much faster.

In order to eliminate this drawback and come closer to large scale plant operations, we have altered the Fischer retort so that the letdown or residue may be injected drop by drop into the retort already brought up to carbonizing temperature. It was hereby found that the yields in the plant and the laboratory are practically the same: 85.5% oil in the laboratory against 83-88% in the plant. For additions of sulfur, red selenium or tellurium the same slight increase in yield was obtained with the altered retort as before.

Though the increase in yield in the carbonization of pitch letdown was unimportant, another effect was observed here, as well as later, in the carbonization of centrifuge residue, i.e. the boiling analysis of the letdown treated without catalyst, compared to the sample treated with catalyst, shows a shift in favor of the middle oil fraction to 300°C. Then, however, the product obtained from pitch letdown treated with catalyst becomes heavier. (See Table 1)

B. Experiments with Centrifuge Residue

After these first experiments with pitch letdown only centrifuge residue from coal hydrogenation was carbonized, also with the altered retort and with superheated steam. With 110 g feed carbonization was limited to 75 minutes with subsequent additional 10 minutes. A series of experiments on the influence of the carbonization temperature indicated that the optimum yield was obtained at 530°C, i.e. at the same temperature used in the plant. (See Table 2).

Experiments were made with four (4) samples, designated I, II, III & IV, taken from the plant on the dates indicated:

I	24 June 1941,	40.5%	solids,	spec.	grav.	1.340
II	23 July 1941	39.5%	"	"	"	1.350
III	23 Oct. 1941	41.5%	"	"	"	1.334
IV	25 Nov. 1941	33.0%	"	"	"	1.243

The results obtained in the carbonization of pitch letdown with catalyst additions were also obtained with centrifuge residue sample I, i.e. alkali or earth alkali hydroxide, metallic oxide, metals and heavy metal salts were a complete failure. We, therefore, worked principally with sulfur and other admixtures to residues II and III.

The slight increase in yield obtained in carbonizing pitch letdown with the addition of sulfur was also obtained here, though to a greater degree, as shown in the comparison of yields with and without the addition of sulfur in the carbonization of samples I, II and III in Table 3. Residue IV was not used for these sulfur experiments, but was carbonized with other additions, later described herein. As to the percentage of sulfur admixture we found that 1.2% is the upper limit. Further addition will do no harm but is useless. Below 1.2% the yield will drop again. (See Table 4)

While we were still experimenting with the residues in the laboratory the plant started to add catalyst to material to be carbonized in July 1941. The laboratory results were herein confirmed, the average yield in June 1941 was 71.5% oil against 79.5% in July. As already mentioned, in the carbonization of pitch letdown it was noted that the addition of sulfur raises the middle oil content, but that above 300°C the oil with sulfur addition becomes heavier. Similar conditions apply to L.T.C. oil from centrifuge residue, except that the entire quantity of the product to 360°C treated with sulfur is increased, as shown in the boiling analysis, Table 5. Table 6 gives results obtained in the plant.

The higher initial boiling point obtained in the laboratory experiments is due to the fact that the aftercooler oil was not treated separately in these experiments, which was done in the plant experiments. The aftercooler oil analyses show more constituents in the fractions between 280 and 360°C with sulfur additions than without sulfur. (See Table 7).

Fluctuations were observed in the fractions below 280°C. Frequently more light constituents were present without addition, which, however, could be charged against our condensation difficulties at the start, particularly with the aftercooler oil, because the still lighter constituents could not be fully liquefied in the catalyst treatment. Recently, conditions here are the same as in the laboratory. (See Table 8).

At times, the yield in the large scale plant experiments would drop, contrary to results in the laboratory with the same material. At first we assumed that the sulfur reacts immediately when added to the residue and is no longer present, or in insufficient quantity, at the entrance to the carbonizing kiln. It was found that temperatures of 70 to 90°C caused a barely perceptible H_2S formation, and that at 110°C traces were observed in treatments up to eight (8) hours. However, at temperatures of 130 to 150°C, i.e. the temperatures used in the plant, a greater decrease in sulfur content could be observed, from 4.0 to 0.8% in 8 hour treatments @ 150°C. The experiments were made gravimetrically quantitative, wherein the H_2S was collected hourly as PbS and weighed after conversion into $PbSO_4$. Table 9 shows the sulfur content after the given time periods. Accordingly, roughly 50% of the sulfur is converted to H_2S after eight (8) hours @ 130°C and roughly 80% @ 150°C.

These experiments induced an investigation in the direction of adding H_2S instead of sulfur to the residue with the result that H_2S is rather somewhat more effective than sulfur:

Residue II, with sulfur, 81.5% oil $^{+3.0\%}_{-4.5\%}$

" H_2S 82.6% " $^{+\,--}_{-0.4\%}$

The above mentioned drop in the L.T.C. yield in large scale operations was, therefore, not due to decomposition of sulfur, but, as we know today, a drop always occurs when the kilns are recycled for lack of feed or because of repairs and are, therefore, shut off and turned on alternately.

These experiments in the laboratory, as well as in the plant, show that the addition of sulfur, as well as selenium and tellurium, increases the oil yield, <u>if superheated steam is used</u>, and that the formation of H_2S in the storage container does no harm. The chemistry of the reaction may even be based on the formation of H_2S which may possibly be converted to split products at the carbonization temperature. For operating reasons, it was also desirable to add soda and sulfigran to the residue in plant operations. However, laboratory experiments with soda showed that the yield is reduced thereby. For example, residue II without any addition yielded 74.5% oil, with 1% soda only 72.0%.

On the contrary, the case is different, if <u>part</u> of the sulfur is replaced by soda. By properly proportioning both, the negative effect of soda can be controlled so that at least the same yield, at times even higher, is obtained as with pure sulfur.

Table 10 gives a picture of the conditions and shows that with 0.15 to 0.3% soda and 0.9 to 1.2% sulfur, based on the centrifuge residue, gives at least the same results as without soda and with sulfur alone.

These experiments were followed by those with additions of sulfigran to the residue, which showed that the yield is increased when small quantities are used, but that larger quantities, above 1.3%, do not affect the yield either way. Sulfigran ranging between 0.3 and 0.9% produced the same yield as sulfur alone, but with 1.3% sulfigran and more the yield approached that without any catalyst. Accordingly, sulfigran may be added without misgivings, particularly since, at times, the yield is even better, when it is used together with sulfur, than with sulfur alone, as with residue II. When using 0.3 to 0.6% sulfigran and 0.9% sulfur, based on the residue, the yield is

83.0 to 84.5%, compared with 81.5% for sulfur alone.

However, conditions are somewhat different with our residue III. The yield here is 82.8% without sulfur, 90.2% with sulfur, but with sulfur plus sulfigran only 86.5% i.e. 4% more than without any catalyst but 4% less than with sulfur alone.

To close the series of experiments we investigated a combination of sulfur, soda and sulfigran. This showed that with not too great an excess of soda and sulfigran the same yields as with sulfur alone may be obtained. This was also tried in the plant by running one kiln part time without a catalyst, with the following results:

Jan. 16 & 19, '42,	76.5%	oil	yield	without	catalyst
" 12 & 15, '42,	87.9%	"	"	with	"
" 20 & 22, '42,	86.5%	"	"	"	"

The composition of the catalyst was:

0.27% soda)
0.30% sulfigran) Based on the residue.
0.30% sulfur)

Which again proves that laboratory and plant agree with each other and that the effect of sulfur is retained with the desired addition of soda and sulfigran.

C - Summary

The entire series of experiments and experiences in the plant definitely showed that with our centrifuge residue the yield is always increased 5 to 10% by adding sulfur and superheated steam, particularly when the sulfur is added, together with soda and sulfigran, in the form of a 20 to 25% paste, as was shown in the latest experiences.

/pkl

TABLE 1

Boiling analysis of the L.T.C. oil from pitch letdown	Without Catalyst	With Catalyst
to 250°C	1.8 %	3.2 %
251 " 300°C	2.5 %	7.6 %
301 " 345°C	26.1 %	24.8 %
346 " 360°C	48.9 %	36.8 %
over 360°C	51.1 %	63.2 %

TABLE 2

Carbonization Temperatures	450°C	470°C	490°C	510°C	530°C	540°C
Oil Yield	60.8 %	67.1 %	69.5%	73.9 %	75.0 %	73.1 %
Additional Coking	34.8 %	28.3 %	24.8 %	17.6 %	18.5 %	18.4 %
Gasification	4.4 %	4.6 %	5.7 %	8.5 %	6.5 %	8.5 %

TABLE 3

Comparison of Yields in Carbonization of Centrifuge Residue with and without Sulfur.

Sample	Yield without sulfur				Yield with sulfur			
	% Oil	% Add. Coking	% Gasification	Deviation	% Oil	% Add. Coking	% Gasification	Deviation
I	74.9	19.0	6.1	+ − 0.1	83.0	8.7	8.3	+ − 1.5
II	74.5	11.4	14.1	+ 2.6 − 1.7	81.5	15.4	3.1	+ 3.0 − 4.5
III	82.8	11.8	5.4	+ 1.2 − 1.2	90.2	6.6	3.2	+ 1.3 − 1.2

TABLE 4

Investigations to determine the optimum amount of sulfur

Residue	Without Sulfur	With Sulfur	
II	74.5 % Oil	0.3 % S	79.0 % Oil
		0.6 % "	79.0 % "
		0.9 % "	81.2 % "
		1.2 % "	84.5 % "
		4.0 % "	85.0 % "
III	82.8 % Oil	0.5 % S	89.9 % Oil
		1.2 % "	90.95% "

TABLE 5

Boiling Analysis of L.T.C. Oil from Centrifuge Residue (Lab. Experiment)

	Without Sulfur	With Sulfur
to 170°C	0.5 %	3.0 %
" 200°C	5.0 %	11.5 %
" 250°C	10.2 %	20.5%
" 325°C	19.0 %	34.5 %
" 360°C	51.5 %	70.5 %
Over 360°C	48.5 %	29.5 %
Spec. Grav./50°	1.052	1.045
Viscosity/50°	5.09°E	3.37°E

TABLE 6

Boiling Analysis of L.T.C. Oil from Centrifuge Residue (Plant)

	Without Sulfur Sample of 6-12	(June 1941) Sample 6-19	With Sulfur Sample of 7-25	(July 1941) Sample 7-31
Initial Boil	328°C	314°C	305°C	326°C
to 320°C	0.0 %	1.0 %	2.0 %	1.0%
" 340°C	1.5 %	2.5 %	7.5 %	3.0%
" 360°C	12.5 %	13.5 %	28.5 %	22.3%
Spec. Grav./50°	1.060	1.069	1.059	1.062

TABLE 7

Aftercooler Oil - Boiling Analyses (Part)

	Without Sulfur		With Sulfur	
	Sample of 6-12-41	Sample of 6-19-41	Sample of 7-25-41	Sample of 7-31-41
280° - 330°C	18.5 %	16.5 %	26.3 %	29.0 %
331° - 360°C	12.0 %	11.5 %	30.0 %	30.5 %
-360° Total	30.5 %	28.0 %	56.3 %	59.5 %

TABLE 8

Aftercooler Oil - Boiling Analyses.

	Without Sulfur		With Sulfur	
	Semple of 6-12-41	Sample of 6-19-41	Sample of 3-8-42	Sample of 3-14-42
Initial Boil.	205°C	134°C	169°C	222°C
to 250°C	34.8 %	33.5 %	59.5 %	15.0 %
" 280°C	52.5 %	48.5 %	69.0 %	55.0 %
" 300°C	58.0 %	56.0 %	72.0 %	72.0 %
" 325°C	68.0 %	65.0 %	76.0 %	88.0 %
" 340°C	73.0 %	67.5 %	80.0 %	94.0 %
" 360°C	82.0 %	76.0 %	86.0 %	98.0 %

TABLE 9

Determination of Sulfur Content in Centrifuge Residue after various periods.

	Experiment at 130°C	Experiment at 150°C
Beginning	4.0 % S	4.0 % S
After 1 hour	3.69 %	3.34 %
" 2 hours	3.41 %	2.79 %
" 3 "	3.15 %	2.33 %
" 4 "	2.91 %	1.95 %
" 5 "	2.69 %	1.63 %
" 6 "	2.48 %	1.26 %
" 7 "	2.29 %	1.05 %
" 8 "	2.01 %	0.80 %

TABLE 10

Comparison of Yields

	Without Additions			With Sulfur			With S + Soda		
	Oil %	Add. Coking %	Gasif. %	Oil %	Add. Coking %	Gasif. %	Oil %	Add. Coking %	Gasif. %
Residue II	74.5	11.4	14.1	81.5	15.4	3.1			
with									
% S + % Soda									
1.2 + 1.8							78.9	12.9	8.2
0.9 + 1.35							81.8	13.4	4.8
1.0 + 1.0							78.4	14.6	7.0
0.6 + 1.0							78.5	16.2	5.3
0.2 + 1.0							78.3	15.6	6.4
0.6 + 0.9							81.5	15.0	3.5
0.6 + 0.5							82.4	14.7	2.9
0.3 + 0.5							82.0	14.8	3.2
0.9 + 0.3							84.6	7.1	8.3
0.6 + 0.3							84.0	5.5	10.5
Residue III	82.8	11.8	5.4	90.2	6.6	3.2			
with									
% S + % Soda									
1.0 + 0.3							90.5	5.8	3.7
0.8 + 0.2							90.6	2.7	6.7
5.0 + 0.15							85.2	10.1	4.7
2.5 + 0.15							86.3	9.2	4.5
1.8 + 0.15							89.8	7.1	3.1
1.5 + 0.15							90.6	7.2	2.2
1.2 + 0.15							92.7	5.8	1.5
0.6 + 0.15							91.3	6.5	2.2
0.4 + 0.15							91.6	7.7	0.7
0.25 + 0.1							88.3	8.4	3.3
0.15 + 0.1							88.5	7.3	4.2

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RECOIL OF HIGH PRESSURE LINE DUE TO A BREAK

Ludwigshafen, May 20,1943

The force acting on a container from which gas escapes is given in Hütte, Vol. I, page 398: (See also Perry, Chem. Eng. Hdbk., 2nd Ed., pg. 846-47, or Kent, Power, 3-77/78).

(1) $K = DV^2F$ (kg)
D = Spec. Mass (kg.sec./m^4)
V = Velocity (m/sec.)
F = Cross-Section of Stream (m^2)

In the end(throat) cross-section of the opening, the pressure of the gas is p_s, where

(2) $p_s/p_1 = (2/m + 1)^{m/m-1}$

m is the discharge (or expansion) exponent (Ausfluss Exponent), approximately $m \approx k$ (kappa) = 1.4 (with frictionless discharge). If the friction cannot be neglected, m is somewhat less than 1.4.

The temperature of the discharging gas in the end cross-section, assuming adiabatic expansion, is given by

(3) $T_1/T_s = (p_1/p_s)^{k-1/k}$

The density of the discharging gas in the end cross-section of the opening then is

(4) $D = \dfrac{S_n \times p_s \times T_n}{C \times T_s \times g} \left(\dfrac{kg.\ sec}{m^4}\right)$

where p_s is the critical pressure in kg/cm^2 and C is the compressibility factor.

Furthermore, according to Hütte, Vol. I, page 553, the discharge velocity

(5) $V_s = \sqrt{2g \dfrac{k}{k-1} \times P_1 v_1 \times \dfrac{m-1}{m+1}}$

or with frictionless discharge

$$(5a) \quad V_s = \sqrt{2g \frac{k}{k+1} \times P_1 v_1}$$

where P_1 is the converter pressure in kg/m^2 and v_1 is the spec.vol. of the gas in the converter (m^3/kg).

Inserting above values for D and V in (1), we get

$$(6) \quad \frac{K}{F} = \frac{s_n \times p_s \times T_n}{C \times T_s \times g} \times 2g \frac{k}{k+1} \times P_1 v_1$$

By substituting

$$y = 1.4$$
$$P_1 = p_1 \times 10^4$$
$$v_1 = \frac{C\ T_1}{S_n p_1 T_n}$$

we get

$$(6a) \quad \frac{K}{F} = \frac{2 \times 1.4}{2.4} \times p_s \times \frac{T_1}{T_s} \times 10^4$$

or with

$$\frac{T_1}{T_s} = \left(\frac{p_1}{p_s}\right)^{\frac{k-1}{k}} = \left(\frac{p_1}{p_s}\right)^{\frac{0.4}{1.4}}$$

and with

$$p_s = p_1 \left(\frac{2}{m+1}\right)^{\frac{m}{m-1}} = p_1 \left(\frac{2}{2.4}\right)^{\frac{1.4}{0.4}} = 0.525\ p_1$$

from this

$$\frac{T_1}{T_s} = \left(\frac{1}{0.525}\right)^{\frac{0.4}{1.4}} = 1.9^{0.286} = 1.2, \text{ and}$$

$$(6b) \quad \frac{K}{F} = \frac{2 \times 1.4}{2.4} \times 0.525 \times 1.2 \times 10^4 \times p_1, \text{ or}$$

$$(6c) \quad \underline{\underline{\frac{K}{F} = 0.735 \times 10^4 \times p_1\ (\text{kg/m}^2)}} \quad p_1\ (\text{atm})$$

If we consider the friction, m < 1.4, assuming m = 1.3, then

$$\frac{p_s}{p_1} = \left(\frac{2}{2.3}\right)^{\frac{1.3}{0.3}} = 0.87^{4.33} = 0.55$$

$$\frac{T_1}{T_s} = \left(\frac{1}{0.55}\right)^{\frac{0.4}{1.4}} = 1.188$$

$$V_s^2 = 2g \times \frac{1.4}{0.4} \times \frac{0.3}{2.3} \times P_1 v_1 = \frac{2 \times 1.4 \times 0.3}{0.4 \times 2.3} \times g\, P_1 v_1$$

$$\frac{K}{F} = \frac{2 \times 1.4 \times 0.3}{0.4 \times 2.3} \times 10^4 \times \frac{T_1}{T_s}\, p_s = \frac{2 \times 1.4 \times 0.3}{0.4 \times 2.3} \times 10^4 \times 1.188 \times 0.55 p_1$$

$$\frac{K}{F} = 0.596 \times 10^4 \times p_1 \quad (\mathrm{kg/m^2})$$

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T-305
W.M. Sternberg

9/23/41

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EXAMINATION, SEPARATION AND HYDROGENATION OF VARIOUS COAL CONSTITUENTS (Data in literature)

Formerly, results of chemical analysis of coal was all that was required. Different structural components possess, however, similar proportions of carbon, hydrogen and oxygen, and the chemical analysis gives no information on their distribution in coal. Within the last years, the petrographic characteristic of coal has been used increasingly in the evaluation of coal. True, the original too high expectations have not been entirely realized; nevertheless, the new method of approach has resulted in a number of new advantages. We can distinguish between the homogeneous and heterogeneous components of coal structure. Anthraxylon (vitrain, Vitrin, Glanzkohle) and fusain (Fusit, Faserkohle) belong to the first, attritus (durain, Durit, Mattkohle) to the second group. The attritus may be composed quite differently, depending on the proportion of its constituents, and may therefore also behive very differently from the chemical standpoint, while in the homogeneous components, the only difference which may exist will result from the difference in the degree of coalification (Kühlwein, Glückauf, vol. 67, p. 1124; Kühlwein, Hoffmann, Krüpe, Ibid., vol. 70, p. 777).

1. The study of structural components is based primarily on microscopic processes (Stach, Kohlenpetrographisches Praktikum, 1928).

Suitably prepared coal is examined with transmitted or reflected light. For examination of the coal in transmitted light it has to undergo the following preliminary treatment:

Ashing of thin splinters of coal by ignition in porcelain crucibles, which leaves behind an ash skeleton, the structure of which is determined under a microscope. This method can not be used with coking coals.

Maceration of coal with oxidizing agents, which will result in the solution of the more readily soluble constituents of the coal and make the more difficultly soluble plant residues visible under the microscope. This maceration is done in chromic acid, or a mixture of calcium chloride and nitric acid, or chlorine dioxide - acetic acid (diphanol).

The most important method for the examination of coal in transmitted light consists in the examination of thin sections, in which a tablet of coal, ground thin enough to become transparent, is examined under the microscope.

Good results are also obtained by the thin section method in which the coal is softened with hydrofluoric acid, imbedded in nitrocellulose and cut with a microtome. Very good thin sections are obtained by this somewhat complicated method, and their microscopy produces good results.

The examination of coal in transmitted light requires overcoming the difficulties of producing thin sections with the added difficulty that coals which fail to become transparent even in thinnest sections can not be examined in this way; accordingly a method for the examination of coals in reflected light has been developed (Stach, Kühlwein, Gluckauf vol. 64, p. 841; Hock, ibid. vol. 67, p. 1126), where coal merely requires being polished. A subsequent etching of the polished section with etching reagents, or a superficial ashing of the surface with a blowpipe permits one to observe the structural elements. A similar relief of polished surface may also be produced by the use of suitable polishing media. Such a coal relief section has the advantage of being readily producible, and may be used with good success on most coals. Stach (Brennstoffchemie vol. 12, p. 147; Lehrbuch der Kohlenpetrographie, 1935) gives several methods for the examination of coal dust sections. The coal particles are solidified by means of some resinous material, wax, or by pressure, and then polished.

The following table gives a survey of the structural components of pure coal. There frequently exist transition stages between anthraxylon, attritus and fusain.

Structural components	Source of origin	Structure	Thin section	Relief section	Appearance.
Anthraxylon (vitrain, bright coal)	Humus (Terrestrial and bog plants, e.g. bark, wood). Passed through a peat and coal formation processes.	Structure frequently absent. If present: wood structure, brittle, breaks down readily into smaller pieces.	Dark red to brown mass	Uniform luster; smooth surface, only broken by characteristic cracks	Bright conchoidal fracture. sp.gr. 1.272 - 1.333
Durain (splint coal)	rotting peat, rich in spores. Spores (occasionally anthraxylon) imbedded in plant material which has lost its structure. Contains more H than anthraxylon. Ash contents varies within wide limits, higher than in anthraxylon, consists of plant ash and foreign clayey ash.	layered; tough, hard.	Spores golden-yellow, transparent	Remains after anthraxylon is abraded; is therefore harder than the former.	Gray-black, velvety black, dull, uneven or conchoidal fracture, layers of ground mass + spores (or small particles of anthraxylon), grow with the layers of anthraxylon. When vitrain is absent then the purest durain; Cannel coal. Sp. gr. 1.295 - 1.492
Fusain	Wood, fossile charcoal. Fusain contains the most ash, compared to anthraxylon and durain (4 - 30%) Higher C content than durain.	Plant cell structure; brittle, readily erased, discolors.	Mostly poor, fusain too brittle, otherwise structure of tissue.	Round cells, thick cellular walls.	Dull, silky luster, gray black-velvety black. Forms narrow layers of pure coal upon layers of hard fusain surface. Cells filled with mineral constituents. Very high in ash. Soft fiber coal; Cells filled with gas. Sp.gr.1.473-1.561

The ash of the coal is not only the ash of the original plant material, but also incrganic minerals and stones, which occasionally are present in an intimate mixture with the coal. Clayey substance is found in the finest layer-like dispersion in the coal. As a rule, fusain has the highest ash, anthraxylon the lowest.

The volatile constituents of the coal largely depend on the structure of the durain, because a higher spore content and other bituminous constituents will result in higher gas contents. The coal becomes more valuable for low temperature carbonization as the bitumen content rises.

---> Decreasing grade of coalification --->

Anthracite	Banded coal	Cannel coal	Boghead	Bright brown coal, tar coal	Brown coal
Layers of vitrain and durain		pure durain	Presumably formed from algae and not from spores	Principally vitrain	Cellular structure
Fusain imbedded between layers Structural details but poorly seen	Structural constituents easier to recognize than in anthracite. 78-98% C. Is usually pure coal. Industrial differentiation: short flame coal, bituminous coal, long flame coal. The coalification decreases from short to long flame coal.	Pseudo cannel coal: durain with narrow layers of vitrain and fusain (transition to banded coals) Cannel coal frequently grades into oil shale.			

The degree of coalification is determined by observing the coal sample in polarized light, because anisotropic properties and reflective power increase with the coalification.

The low coalification grades of short flame coal permits ready distinguishing of its structural constituents, because they have suffered the least change in comparison with the other grades of coal.

Spores, cuticle, etc. are well preserved in the bituminous coal but less so than in the long flame coal.

Changes in the bituminous substances are already very pronounced in the bituminous coal, which for that reason is considerably less readily identified.

Durain is least readily recognized in the short flame coal, because the coalification of the spores and other bituminous materials has progressed the farthest.

The petrographic composition alters from the long flame coal to the short flame coal. One may find the following average values in the Ruhr coal:

Contents on:	durain	bright coal	fusain	Mineral constituents
(Gasflammkohle) Subbituminous coal	25%	abt. 65%	3.6%	↑
(Gaskohle) Long flame coal	25%		3.6%	
(Fettkohle) Bituminous coal	13%	↓ Increases	2.9%	increase
(Magerkohle) Short flame coal	7%	abt. 90%	2.3%	slight

2. Separation of the coal constituents from each other may be realized in a variety of ways. Simple screening is impractical, because the grain size of vitrain and durain is about the same in ordinary grinding, because of their small difference in hardness. On the other hand, comminution by an elastic shock should produce sufficient differentiation in grain size. (Hoffmann, Glückauf, vol. 66, p. 536; Lehmann Proc. 3-rd Intern. Confer. Bit. Coal, 1931, vol. II, p. 686). The limit of elasticity of the bright coal is exceeded with the suddenly produced elastic shocks, while the stronger dull coal withstands them for a longer time, and merely tends to soften the blows. The coarse fraction becomes enriched in dull coal, the finer fraction in bright coal. The strength and hardness of the dull coal increase with increasing bitumen content. Fusain is mostly found in the finest fractions.

The bright and dull coals have approximately equal specific gravities, while fusain has a much greater specific gravity, and this may be used as a basis for their separation. The sink and float process produces good results, and is the most frequently used process (Raub, Glückauf, vol. 75, p. 101; Gotte, ibid., vol. 72, p. 738). The separation is made in heavy solutions (carbon tetrachloride + xylol, or bromoform for spec. gr. in excess of 1.6). The higher ash content of the fat coal introduces however frequently great uncertainties in the separation (Stach, Internationale Bergwirtschaft und Bergtechnik, 1930, p. 259).

Dull and bright coal can not be well seperated by this process. An example of the sink and float separation is shown in the table below (Raub, loc. cit.)

Sp.Gr.	Percent floating constituents					% sunk material
	vitrain	clarain	durain	transit. and fusain	shale	
1.9	42.3	26.4	5.8	7.0	9.3	9.2
1.8	42.3	26.4	5.8	7.0	7.9	10.6
1.7	42.2	26.4	5.7	6.9	6.7	12.1
1.6	41.1	26.2	5.5	6.5	5.8	14.9
1.5	40.5	25.5	5.3	6.1	3.9	18.7
1.4	38.2	25.2	4.7	5.3	1.1	25.5

A modification of the sink and float method is the centrifugal sink process, in which the separation is also produced in heavy solutions, and the sinking of the particles greatly accelerated by centrifuging. In addition, centrifuging brings about a sharper separation of the structural components.

There are uncertainties in the sink and float process, resulting from the appearance of boundary surface forces from the occluded and adhering air bubbles, and air has accordingly been tried instead of liquids. The coal is raised with air, and the smaller particles carried away with a stream of air. The desired object has however not been achieved with air classification.

Finally, the constituents could be separated from each other on the strength of their different electrical conductivity (Stach, Internationale Bergwirtschaft und Bergtechnik, 1930 p. 259). The electrostatic coal separation can however be used only with fusain. The conductivity of fusain is greater than of the other constituents, and the fusain is pulled out by applying an electric field, and then removed with a stream of air.

All these methods of separation result only in an enrichment of one single constituent, and the separation is never perfect.

According to Hoffmann (Glückauf, vol. 66, p. 529) bright coal is best suited for coking, the dull coal for hydrogenation, low temperature carbonization and gasification, and fusain for powdered coal combustion. According to Kühlwein (Glückauf, vol. 70, p. 994) the hydrogenating coal must be free from fusain and much opaque attritus, while the durain must be high in prebitumens. The composition of durain may be recognized by its gas content. In the presence of a high proportion of opaque constituents in durain, the gas content is below that of the layer vitrain, while with a high prebitumen content it is considerably above it.

3. Hydrogenation

Storch and collaborators studied the hydrogenation of the different components of the structure of anthraxylon (Ind. Eng. Chem. vol. 31, p. 1155; Fuel, vol. 18, p. 196).[1] The hydrogenation was done at an initial temperature of 20° and a reaction temperature of 430° under 7 atm pressure for 3 hours in a solution of tetraline and in the presence of SnS.

All samples containing less than 89% C were hydrogenated with a good yield. All anthraxylons gave better yield than splint coal of the same

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[1] The English designation "anthraxylon" for one of the components of coal structure does not quite correspond to our (German) definition Glanzkohle (bright coal) or vitrain (vitrit), but seems to come close to it. Neither is the German terms "Mattkohle" or "Durit" quite the equivalent of "attritus", which is more of a definition of the groundmass which may be either transluscent (limited coalification) or opaque (high degree of coalification). The English fusain corresponds to the German "Fusit". The coal bands (banded coal) are composed of splint coal (Schieferkohle) and bright coal (Glanzkohle), which consist of the following structural constituents: splint coal: 20-35% anthraxylon, the balance attritus (principally opaque), fusain, etc. Bright coal: 50-75% anthraxylon, balance attritus (principally transluscent), fusain, etc.

carbon content. The opaque constituents furnish difficulties in hydrogenation, while spores, cuticle and resinous materials are readily hydrogenated. For this reason, high rank coals are poor hydrogenation coals, those rich in spores and resin are good. Anthraxylons of low coalification give hydrogenation yields of 95 - 99%. The tars produced are higher in H and C than the original coals; the C:H ratio is however lower. The residue is not opaque, unlike that of fusain and splint coal.

Hydrogenation of Attritus. Ind. Eng. Chem., vol. 31, p. 1155; Fuel, vol. 18, p. 132. The transluscent attritus behaves in hydrogenation approximately like anthraxylon of low C content (low coalification). Pure spores and cannel coal can therefore be readily hydrogenated. Pollens and the other plant residues behave similarly.

Conversely, opaque attritus gives, like fusain, the lowest yield in hydrogenation. This might have been expected because of the opaqueness and the high C:H ratio. The hydrogenation yield was here only 62%. 21 - 63% of the opaque material was retained as not capable of hydrogenation. The hydrogenation residue is always directly proportional to the opaque matter. Opaque attritus does not correspond to the fusain, because the characteristic fibrous structure is absent in it; the hydrogenation residue of the two coal constituents are also different.

The tars and viscous oils obtained have a lower C:H ratio than the original coal, but it is roughly proportional to the latter. Tars obtained in the hydrogenation of spores and resins had a higher hydrogen and lower carbon content. The C:H ratio of the hydrogenation residue was higher than in the original coal.

Hydrogenation of fusain (Ind. Eng. Chem., vol. 31, p. 190)

The hydrogenation of fusain was surprisingly better than expected. In some cases yields as high as 25% have been obtained.

One may judge approximately how far hydrogenation will proceed from the C and H content, the C:H ratio, and also from the volatile matter content.

Fusain is up to a point readily hydrogenated, but more difficultly beyond that. The tars obtained had in all cases a lower C:H ratio than the original coal. The principal product was the insoluble residue. In it, the C:H ratio was higher than in the original fusain. The insoluble residue contains more volatile constituents.

The C content of a coal increases with progressive coalification, and the hydrogenation capacity of coal can to a certain extent be predicted from its C content. This is primarily true for homogeneous bright coal, principally composed of anthraxylon. The conditions with splint coal (principally attritus) are more complicated; their carbon content has an intermediate value, which depends on the proportion of spores and other bituminous materials, and is no measure of the opaque matter and fusain content. The same applies to the C:H ratio and the proportion of volatile matter. Petrographic determinations must in this case be made use of. It may however be assumed, as a rough approximation, that the C content, the C:H ratio and the difficulties of hydrogenation increase with the proportion of the opaque matter. The semi-opaque matter can still be hydrogenated under more drastic hydrogenation conditions, and the hydrogenation yield is then increased.

The properties of the hydrogenated products depend on the raw material. Thus, specific gravity is the lower, the higher the spore and resinous matter content are.

Hydrogenation of Splint Coal (Ind. Eng. Chem., vol. 32, p. 73; also Fuel, vol. 18, p. 196) of the following petrographic compositions:

No. of sample	% anthraxylon	% Attritus translucent	opaque	% Fusain	% not hydrogenated in the original sample 1/
1	24	37	34	5	21
2	13	52	33	2	46
3	3	35	60	2	57
4	17	50	31	2	56
5	9	38	51	2	27
6	8	41	50	1	44
7	8	45	46	1	44
8	13	32	50	5	61

1/ The assumption is made, that everything, except the last column and fusain is hydrogenated.

The hydrogenation of splint coal gave lower yields, which confirmed the opinion that splint coals are not well suited to hydrogenation, because their principal constituent is the opaque attritus. Whenever splint coal contains but little opaque matter, its hydrogenation again becomes easier. The transformation into gases, liquids, and soluble materials amounted to 58 - 87%. This yield is lower, than in the hydrogenation of bright coal, spores, resinous matter, transluscent attritus and anthraxylon. The C:H ratio of the tars produced was always higher than in the original coal, but lower than in the residue from the hydrogenation of fusain. No spores nor resinous matter is found in the benzol insoluble residue, which shows that they have been hydrogenated.

Unlike the American investigators, the Germans have found that splint coal is more readily hydrogenated than bright coal. All agree, however, that a structure constituent rich in spores and bituminous matter of low gasification is better suited to hydrogenation than a material high in opaque matter, i. e. one which has far progressed in coalification, and it may be assumed that the differences are merely a result of the non-uniformity in the classification of the coal structure constituents.

/s/ Henkels

Supplement to the compilation "Examination, Separation and Hydrogenation of Various Coal Constituents", of 9/23/41.

9/26/41.

Hoffmann and Kühlwein, Glückauf, vol. 71, p. 625 give chemical analyses of a few assumed structural constituents of a Saar colliery, which are summarized in the adjoining table. The table contains in addition the yields of tar from the coal constituents from the same mines.

This permits to compare a certain constituent of one coal with another constituent of the same coal. One finds in most cases more carbon and hydrogen and less oxygen in durain than in vitrain.

The yields in tar are throughout higher from the attritus than from bright coal, which is connected with the higher prebitumen content. The tar yield is, moreover, dependent on the granulation.

/s/ Henkels.

/fkp

Mine	Ultimate analysis						Oil and Tar Yield							
	vitrains						vitrain				durain			
							L.T.C. 1)		Coking 2)		L.T.C. 1)		Coking 2)	
	C %	H %	O %	N %	S %	g H/ 100g C	0.5 mm %	4900 M/cm^2 %	0.5 mm %	4900 M/cm^2 %	0.5 mm %	4900 M/cm^2 %	0.5 mm %	4900 M/cm^2 %
1	82.42	5.22	10.69	1.08	0.59	6.35	14.93	15.97	7.23	8.23	33.05	34.11	16.26	17.47
2	83.77	5.62	8.98	0.96	0.67	6.72	12.52	12.80	7.19	8.24	28.98	31.13	14.00	15.07
3	84.55	5.13	8.44	0.99	0.89	6.07	13.31	13.93	8.51	8.38	26.07	27.	16.36	16.07
4	84.93	5.31	8.38	0.88	0.50	6.27	12.69	14.19	6.84	6.17	22.14	26.78	13.82	17.70
5	85.30	4.95	7.76	1.13	0.86	5.8	12.39	13.15	6.95	7.64	16.53	18.86	9.83	12.00
6	85.31	5.47	7.64	0.99	0.59	6.41	12.01	12.66	9.57	8.94	16.14	20.56	12.35	14.49
7	85.57	5.28	7.06	1.33	0.76	6.18	11.96	12.55	6.77	6.55	20.91	20.08	8.92	12.59
8	86.01	4.99	7.05	1.26	0.69	5.8	11.96	12.63	6.50	6.12	19.62	20.37	9.94	11.22
9	86.08	5.27	7.00	0.94	0.71	6.13	12.41	12.76	7.08	7.62	18.37	20.14	11.15	14.00
10	87.24	5.01	6.28	0.76	0.71	5.75	12.70	13.48	8.60	8.39	14.89	15.17	10.09	10.75
11	87.28	5.23	5.29	1.44	0.76	6.	13.41	13.84	6.93	7.02	--	--	--	--
12	87.97	5.24	5.07	1.06	0.66	5.97	13.15	12.77	7.58	6.79	16.73	18.66	11.05	12.55
Mittel	85.54	5.23	7.47	1.07	0.70	6.12								

1-4 young flame coals, the durain in which contains much prebitumen.

1) At 550° according to Fischer, in an Al retort, distillation time 45 mins.
2) At 900° according to Bauer, distillation time 75 minutes.

T-306
W.M. Sternberg

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

TOM Reel 170 - Frames 124 - 132 Sept. 6, 1941

THE EXTRACTION, HYDROGENATION, COKING AND DISTILLATION BEHAVIOR OF DIFFERENT COAL CONSTITUENTS

An extract from several earlier works from the Kaiser Wilhelm Institut für Kohlenforschung in Mülheim-Ruhr.

Summary:

1) The attritus from a Ruhr bituminous coal gives with different extraction media at ordinary pressure 60 - 70% of the extract which can be obtained from anthraxylon of the same coal. When extracting with benzol under pressure, the differences are less (90%).

2) In the hydrogenation under very mild conditions (215°, 180 atm hydrogen), 10% of the attritus coal and 15.8% of the anthraxylon is converted into benzol soluble products.

3) The porosity of coke from attritus is very slight, that of anthraxylon very strong. The porosity of coke from anthraxylon is much more reduced by the addition of attritus than would follow from the law of mixtures.

4) The very different behavior of bright coal and attritus during the low temperature carbonization and coking is principally determined by the insoluble residue, while the soluble bitumen of the anthraxylon and attritus affects similar coking properties.

5) Anthraxylon is more rapidly oxidized than the attritus, and it combines with a greater amount of oxygen than the attritus.

/s/ Peters

More tests were made with the Ruhr bituminous coal of the Matthias Stinnes mine of the following composition:

Ultimate analysis	Welheim analysis	for purpose of comparison: coal K 1068: analyses	Stinnes Leuna
% Vol. Matter -	-	29.16	29.91
C	35.84	87.70	87.12
H	4.63	5.16	5.29
O	7.93	3.80	4.85
N	-	2.33	1.81
S	-	1.03	0.93

1). Extractions 1/.

Coal for extraction samples was always pulverized in vacuum ball mills to μ size, and extracted at the boiling point of the solvents.

Extraction of Coal Constituents.

Samples of the constituents were hand picked from the Matthias Stinnes bituminous coal. The petrographic composition of the three samples is summarized in the following table:

Sample	% bright coal	% splint coal	% fusain	% gang
Anthraxylon	92	4	2.5	1.5
Attritus	18	80	2	-
fusain	15	3	73	9

The structural constituents ground to μ fineness gave the following extraction values when extracted with different solvents:

Solvent	banded coal	anthraxylon	attritus	fusain
1) trichloethylene	10.6	12.1	7.5	2.9
2) Benzol	8.1	8.2	4.8	2.5
3) Benzol under press.	6.9	9.3	8.6	-
4) carbon disulfide	7.5	9.0	6.3	3.2
5) benzol, after CS_2	2.0	0.3	-	1.4
6) sum of 4) and 5)	9.5	9.3	6.3	4.6

These figures show that the extraction yields are reduced progressively from anthraxylon through the attritus to fusain, regardless of the solvent.

2) Hydrogenation 2/.

Coal samples, ground to μ fineness were heated in the presence of molybdenum catalysts in a benzol suspension in a shaking autoclave and under compressed hydrogen to temperatures below the decomposition temperature of coal. The reaction mixture was next extracted under normal pressure with benzol. With sufficiently long time of hydrogenation most of the coal can in this way be converted at 200 - 285° C to benzol soluble products.

Anthraxylon and attritus (picked from the Stinnes coal) were hydrogenated in this way for 96 hours each at 215°C, with hydrogen under a pressure of 180 atm. 15.6% extract was in this way obtained from the anthraxylon and 10% from attritus.

3) Coking and Low Temperature Carbonization 3/.

The following values show the relationship between proportion of anthraxylon and attritus upon the volume increase during coking:

Coal	Proportion of Anthraxylon %	Proportion of attritus %	Degree of swelling Lambris	Degree of swelling calcul.	Factor for the deviation from the mixing proportion
Matthias Stinnes Mine coal	-	100	1.8	-	-
	50	50	2.0	9.5	0.22
	60	40	4.5	11.0	0.41
	65	35	4.5	11.9	0.38
	70	30	6.5	12.6	0.52
	75	25	9.0	13.4	0.68
	80	20	9.5	13.6	0.72
	85	15	11.0	14.7	0.75
	100	-	17.2	-	-

All degrees of swelling of mixtures of anthraxylon and attritus during coking are much below the ones calculated from the law of mixtures and which should be located on straight lines of the swelling of mixtures. The deviation from the law of mixtures is greatest with about equal proportion of anthraxylon and attritus. One may also observe the smaller amount of swelling with the fine ground coal, than with coarser grains of the Stinnes mine bituminous coal, as has already been pointed out in the first communication on the ground coal, and which is not observed with other bituminous coals (Westfalian mines). The deviation from the law of mixtures may be expressed by the factor

$$f = \frac{V\ \text{found}}{V\ \text{determined}}$$

The V in this formula represents the volume of coke found in the Lambris test, and that calculated from the law of mixtures by the formula $V\ \text{calc} = \frac{aV\ \text{anthr.}}{100} + \frac{bV\ \text{attritus}}{100}$, where a and b are the percentages in the mixture. The fact, that even a small addition of attritus reduces swelling by more than corresponds to the law of mixtures finds its expression in the smaller value of f, than 1.

This phenomenon is similar to the lowering of the melting point of mixtures of two substances which is generally observed. The lowering of the swelling may well be based on the fact, that in temperature ranges, at which the swollen anthraxylon solidifies, the anthraxylon + attritus mixture still remains so soft, that the gas bubles burst, which results in the formation of a less porous coke.

If bitumen is removed from coal by extraction, the degree of porosity of the coal drops as follows:

Degrees of Porosity of Bituminous Coal, Extracted with Benzol

Bitumen extracted from coal, in % of the coal	Volume of coke from extracted coal, Lambris	Bitumen extracted from coal, in % by weight of the coal	Volume of coke from extracted coal, Lambris
0	10.9	5.5	5.3
1.6	9.9	5.9	4.8
2.6	9.1	6.8	4.7
3.9	7.1	7.5	3.1
4.0	6.1	7.8	2.0
		8.5	1.5

When such tests are performed with pure anthraxylon, it is found to behave quite similarly to banded coal. The drop in the baking ability becomes very noticeable in attritus when over 3% bitumen has been extracted from it.

When bitumen is again added to completely extracted coal, the baking and porosity increase properties are restored.

Nature of the coal	Volume of coke, in m^3 Lambris Stinnes mines	 Westfalian mine
Not extracted Anthraxylon	12.8	15.7
Not extracted attritus	1.8	2.6
Extracted anthr. with added bitumen from anthrax.	12.4	14.2
Extracted anthr. with added bitumen from attritus	9.1	11.6
Extracted attritus with antraxylon bitumen added	2.0	1.7
Extracted attritus with attritus bitumen added	2.0	2.4

The anthraxylon bitumen causes a greater increase in porosity than the attritus bitumen. The coking properties are never-the-less primarily determined by the properties of the insoluble residual coal.

4.- Oxidation 4/.

The following tests with picked anthraxylon and attritus samples from the Stinnes mine coal were made to get information on the difference of oxidizing power of the different structural constituents. Seven samples of anthraxylon and attritus constituents were ground in a vacuum ball mill and kept, the same as all the other samples, in well ground ground-glass stoppered bottles to protect them against oxidation or any other changes in the air. For the test they were oxidized in air by heating them in crystallizing dishes in an electrical drying oven at 110°. The gain in weight was determined on an analytical balance every two or three days for a total of six weeks, and 5 samples of 0.7 g.

each were taken for the determination of the heating value. The results are reproduced in the following column:

Heating Values of Oxidized Anthraxylon
and attritus, in percent of Heating
Value of the Original (Unoxidized) Coal.

Days of oxidation at 110°	Anthraxylon Heating value cal./g	%	Attritus Heating value, cal./g	%
0	8437	100.0	8300	100.0
1.6	7775	92.0	7905	93.3
13.3	6870	81.5	7110	85.9
22.3	6740	79.8	6985	83.3
42.0	6650	78.9	6910	83.2

Increases in Weight of Structural Constituents
During the Oxidation in the Drying Oven,
Referred to Unoxidized Coal

Days of oxidation at 110°	Increases in Weight, in % Anthraxylon	Attritus
0[x]	0.00	0.00
0.6	1.20	0.80
1	1.60	1.20
1.6[x]	2.30	1.80
2.3	2.70	2.10
4.4	4.20	3.30
8.4	5.20	4.00
11.3	5.85	4.70
13.3[x]	5.70	4.75
15.3	6.10	5.00
17.3	6.10	4.97
20.3	6.20	5.10
22.3[x]	6.40	5.25
24.0	6.90	5.80
27.0	6.80	5.70
30.2	6.80	5.80
42.0[x]	7.20	6.05

[x] Heating value determinations were made after these time intervals.

The table shows, that both kinds of coal constituents, as well as the banded coal mentioned above, absorb appreciable amounts of oxygen at 110°. The increase in weight is large during the first four days, amounting to 3 to 4%, while after some 40 days more they acquire a total of 6-7%. In agreement with older observations, made with English coals, anthraxylon absorbs oxygen more rapidly and in larger amounts, than attritus.

As the weight increases, the heating value of the coal structure constituents decreases. The drop in the heating value, referred to the heating value of the original unoxidized coal, reaches 21.0% in anthraxylon and 17% in attritus. During the whole length of the test, the loss in the heating value, expressed in %, is always two to three times as great as the weight increase of the coal in percent. The oxidation which finds an expression in the increase in weight and the drop in the heating value, proceeds more rapidly at first, than slows down. It is however not over even after weeks of test.

/s/ Peters

1/ Brennstoffchemie, vol. 13, 1932, pp. 364-370

2/ Ibid., vol. 14, 1933, pp. 181-184

3/ Ibid., vol. 14, 1933, pp. 445-450

4/ Angewandte Chemie, vol. 46, 1933, p. 498.

Supplement:

No hydrogenation tests are available with structure constituents from the same coal. A Brassert coal broken down into its constituents by Dr. Lohmann, had the following composition of these constituents:

	Anthraxyl. I	Anthraxyl. II	Attritus	Fusain
% ash, maf coal	1.45	3.79	5.77	13.11
% C, maf coal	87.12	87.52	86.84	86.70
H	5.16	5.13	4.96	4.76
O	6.32	5.85	6.61	6.69
N	0.56	0.58	0.62	6.85
S volatile	0.84	0.92	0.97	1.00
S total	0.93	0.97	1.11	1.19
avail. H/100 g C	4.84	4.83	4.54	4.25

Translator's note: The following terms were used in this translation:
Banded coal for Streifenkohle
Attritus for Mattkohle
Anthraxylon for Glanzkohle
Fusain for Faserkohle

See footnote in T-305 for a comparison of the terms

./pkl

c1+ Eq.

Storch

667 T-307

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

KCBraun
4/4/47

EMERGENCY EXPANSION - DECOMPRESSION (NOTENTSPANNUNG) OF HYDROGENATION STALLS

Leunawerke, 8 October 1942

1. Rise of Temperature in the Converters.

Number of Measuring Points, (based on the type of converters in use at present):

Liquid Phase Converter, (coal stall, 200 atm):
1 - 2 in cover, 3 jacket elements, 1 element in converter inlet, 8 converter elements, of which 2 in converter I and 1 in converter II are resistance elements.

Prehydrogenation Converter, (200 atm, tray converter):
2 x 2 in cover, 3 jacket elements, 1 element in converter inlet, 1 element in the upper part of the first catalyst layer, as well as 1 element in each catalyst layer and 1 element below. The number of elements is, therefore, dependent upon the number of catalyst trays. With the generally abandoned flow from bottom to top the gas space elements are above the corresponding catalyst layer. At times, there is a resistance element in the outlet of converter I.

Benzination Converter, (200 atm, tray converter):
Cover and jacket as above, also elements in the catalyst and below the trays. Additional element in converter I inlet as above and in converter IV outlet. A vapor phase converter with 4 trays, therefore, has 9 elements, at times a 10th in the outlet. A converter with 6 trays has 14 to 15 elements.

Recorded are:

Liquid Phase: 1 - 2 elements each converter, converter inlet on each converter, also preheater and heat exchangers both passes inlets and outlets.

Vapor Phase: As above, except that the converter inlet is usually recorded only for converters I and II.

Converter Operators:
Each stall (liquid and vapor phase alike) has 2 men, relieved every 6 hours (12 hour shift). One man runs the stall, the other does the clerical and catchpot work.

Time required to record all elements:

a) - Liq. Ph. & Vap. Ph. Conv. without trays, 1/4 to 1/2 min.
b) - Vapor Phase Converter with trays, 1/2 to 3/4 min.

Special Remarks:

No conclusion can be drawn of the speed with which any trouble can be recognized from the time required to record all the elements of a converter. The moment in which an operator notices an irregularity and the period of time required to recognize the cause of any trouble depends too much upon the attention and intelligence of the man in question. To this must be added, that, in case of trouble, there should be no difference in the time required to judge the condition of this or that type of converter, because in an emergency the experienced operator will read only his major control elements and, in the vapor phase tray converter, e. g. only the elements in the catalyst.

Time required for a stall to run away:

a) - Liquid Phase, 4 min.
b) - Vapor " , 3 " .

2. **Observations on the progressive temperature rise.**

Fire in stall 2 due to sudden change of injected feed and subsequent rise in temperature.

The stall in question was a B-product stall in which the temperature rose so fast that the connecting pipe between converters I and II burst within 4 - 5 min. after the rise was first noticed. Fig. 1 shows the temperature rise in converter I.

3. **When to expand in an emergency.**

Instructions for emergency expansion are available only for the vapor phase:

@ 24 mV cut injection immediately to half.
@ 26 mV cut out injection entirely immediately.
@ 30 mV shut oil pressure valve in circulating line and expand over 45 mm valve 9.

The normal temperature of the vapor phase is 18 to 23 mV. Cold gas is used to depress the temperature.

Liquid phase coal stalls are expanded only in case of defective equipment or fire in the stall.

The normal temperature of the coal stall is between 24 and 26 mV. As soon as a rise in temperature can no longer be controlled by cold gas, the injection into converter I

(28 to 32 m^3/h) is reduced by 5 m^3 at 27 mV and pasting oil is injected. This procedure has so far been enough to prevent a further rise in all cases. If it can't be applied in time the stall will coke up. If there is reason to believe that the stall has been damaged by the rise in temperature, it is changed over entirely to pasting oil and de-sludged in the usual way, although generally faster.

4. How to expand in an emergency.

Emergency expansion in both liquid and vapor phase consists merely in shutting off injection, shutting the oil pressure valves (pressure and suction side) and opening expansion valve 9. The procedure then immediately followed for the coal stall is described below:

Fig. 2: (Arrangement of expansion and letdown lines)

All valves are hand operated, except that in the de-sanding line from converter I there is a quick-closing valve (oil pressure), because of the danger of erosion in this line.

All letdown valves are 30 mm. The valves at the pit are normally open. No expansion tower is available, but one pit with auxiliary expansion pot for 4 to 6 coal stalls.

The distance of the pit from the stall is 70 m, from the operating stand 60 m.

For each stall are available: 2 letdown lines, each with 2 - 30 mm valves at the pit, 2 - 30 mm valves for each converter in the stall valve group, as well as 2 - 30 mm valves at H. E. II, and 2 each on the intermediate catchpot and the cold catchpot. The normal letdown can also be diverted to the pit by a valve.

Sequence of Operations.

First, the pit valves are closed and the lines from the stall to the pit are compressed with N_2 @ 200 atm. The stall is then de-sludged in the following sequence:

The hot catchpot is emptied in the normal way. Then the cold catchpot and the intermediate catchpot are emptied into the pit (or normally, if possible), followed by de-sludging the converters from IV to I and heat exchanger II last.

The sludge is let down at present only after the stall has been cut off the circulating line. The above mentioned sequence is based on the necessity of avoiding, e.g. that in de-sludging converter I, the residues still contained in the other vessels flow back and cause uncontrollable mixtures.

The letdown lines are of N6 material and 30 mm dia. No defect has, so far, been detected in them. They run in the pipe trench from the stall valve group between the operating stands to the letdown group and pit. As mentioned above, they have 2 shut-off valves, which are open when the stall is operating and are, therefore, without pressure.

When a converter is completely de-sludged the valves at the converter are closed again.

As soon as a stall is completely de-sludged, the lines are blown out with N_2 and decompressed.

Finally, attention should be called to the necessity of avoiding mixtures by continuously injecting a little flushing gas into the individual converters and heat exchanger II (about 50 m^3/h each) thru the letdown openings by way of the letdown lines. A little gas must also be run thru the heat exchanger coils as soon as the stall is run without injection.

Discussion with Rheinbraun, 6 July 1942

Becker, Leuna:

When the temperature in a vapor phase stall is 2 mV higher than normal injection must be cut off.

Schappert:

Temperature Rise	Time in which temp. rises
From 25 to 26 mV	3 min.
" 26 " 27 "	1 1/2 min.
" 27 " 28 "	1/2 min.
Above 28 mV	seconds

Emergency expansion to 100 to 150 atm requires abt. 6 min. with 4 converters.

Peukert:

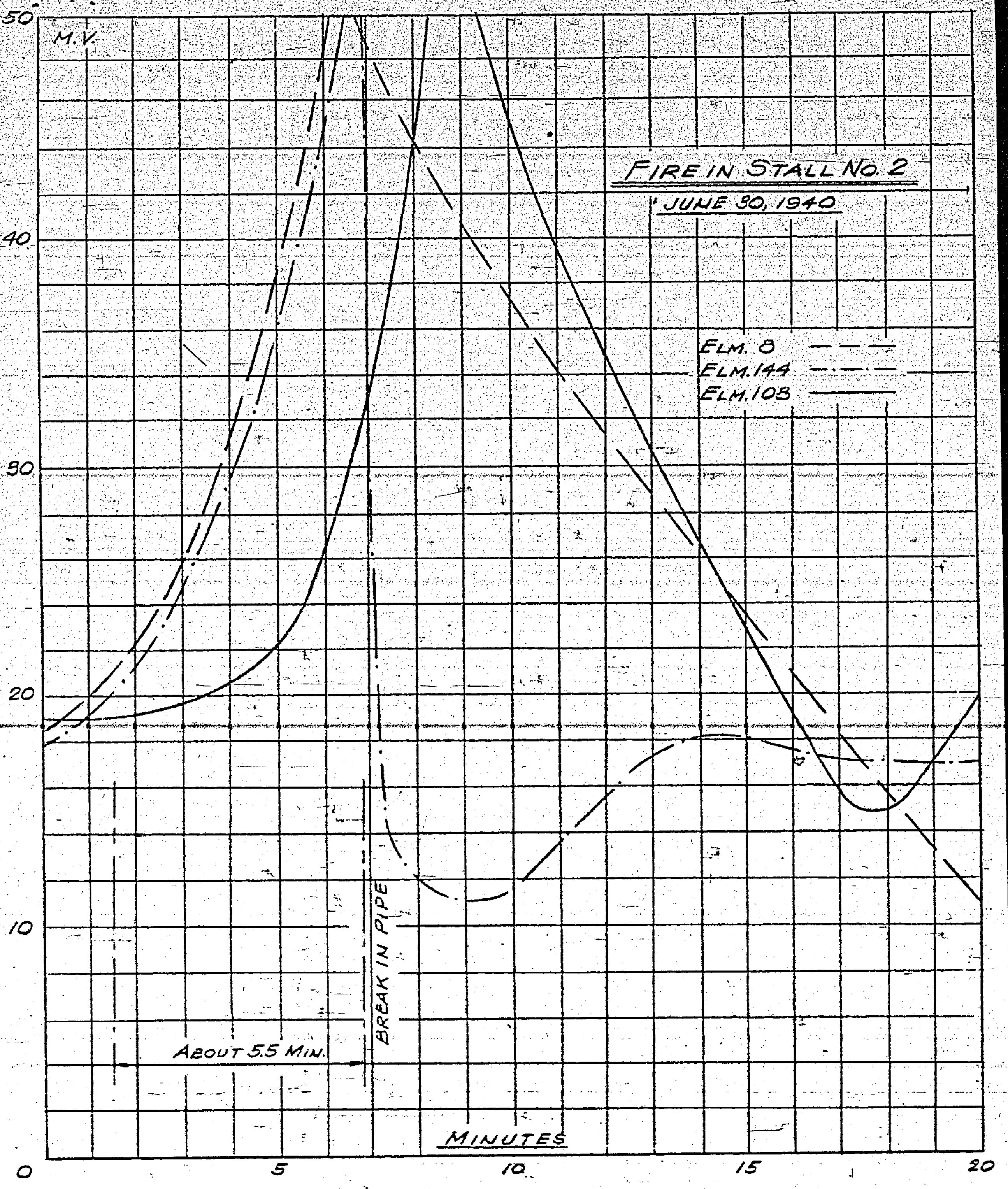
If it is left to the judgment of the operator to de-sludge after an element, liquid phase converter, has automatically indicated 27 mV, there will, in all probability, be no trouble. All converters should be decompressed at the same time.

In Rheinbraun an element will rise locally due to caviar coking. The general rule can, therefore, be applied only to bituminous coal stalls.

In an emergency letdown the gas must be released to the atmosphere at the same time. This is always done in Rheinbraun when there is danger. The gas always spits some when released under pressure. The disadvantage in this is that the contents of one converter may be drawn over into an other converter. The letdown line should not pass the operating stand, because of the danger of bursting of such a line.

/mc

FIG. 1


FIRE IN STALL NO. 2
JUNE 30, 1940
M.V.
ELM. 8
ELM. 144
ELM. 108
BREAK IN PIPE
ABOUT 5.5 MIN.
MINUTES
0
10
20
30
40
50
5
15

T-307

Arrangement of Letdown Lines

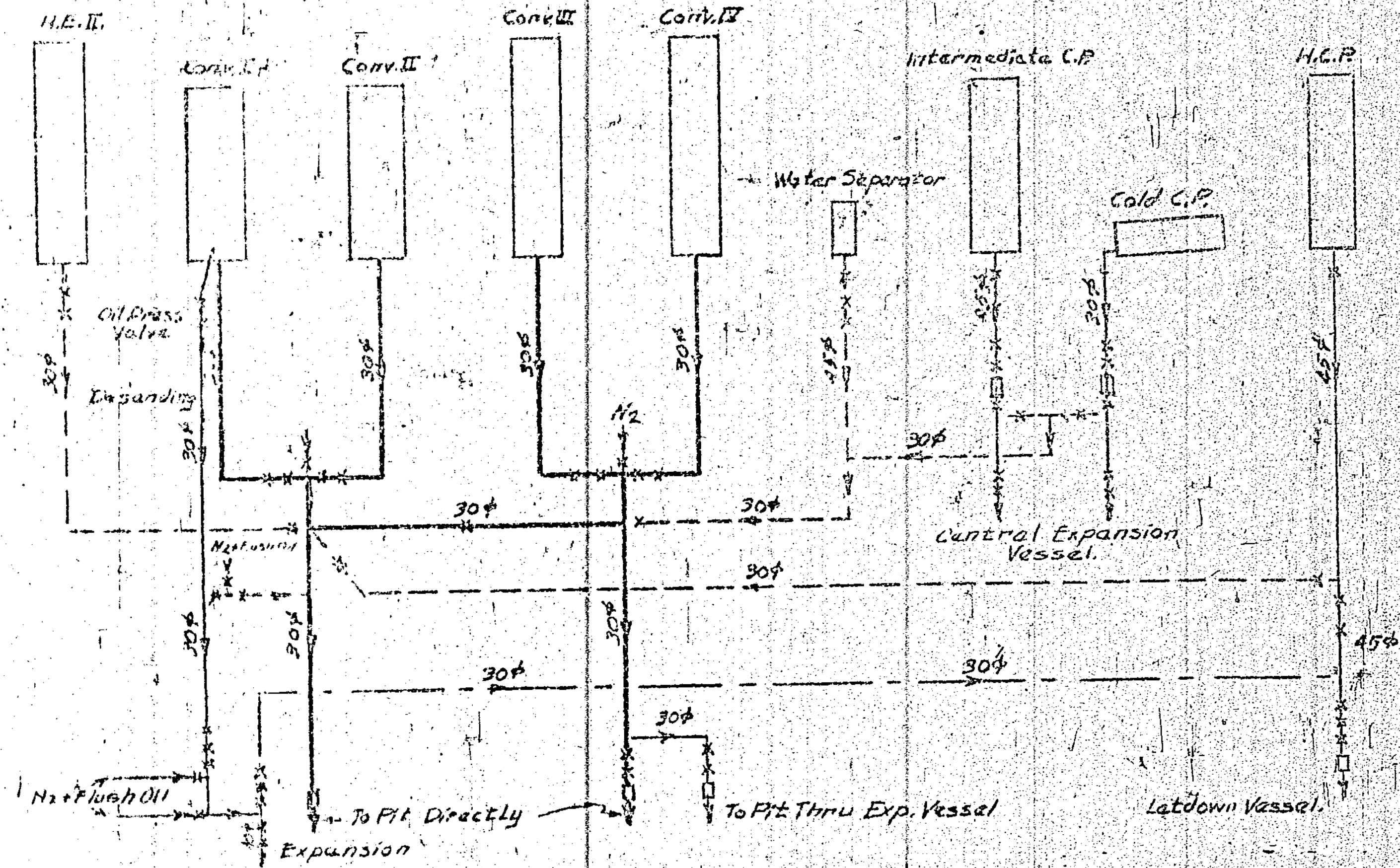


FIG. 2

U. S. BUREAU OF MINES
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674 T-308

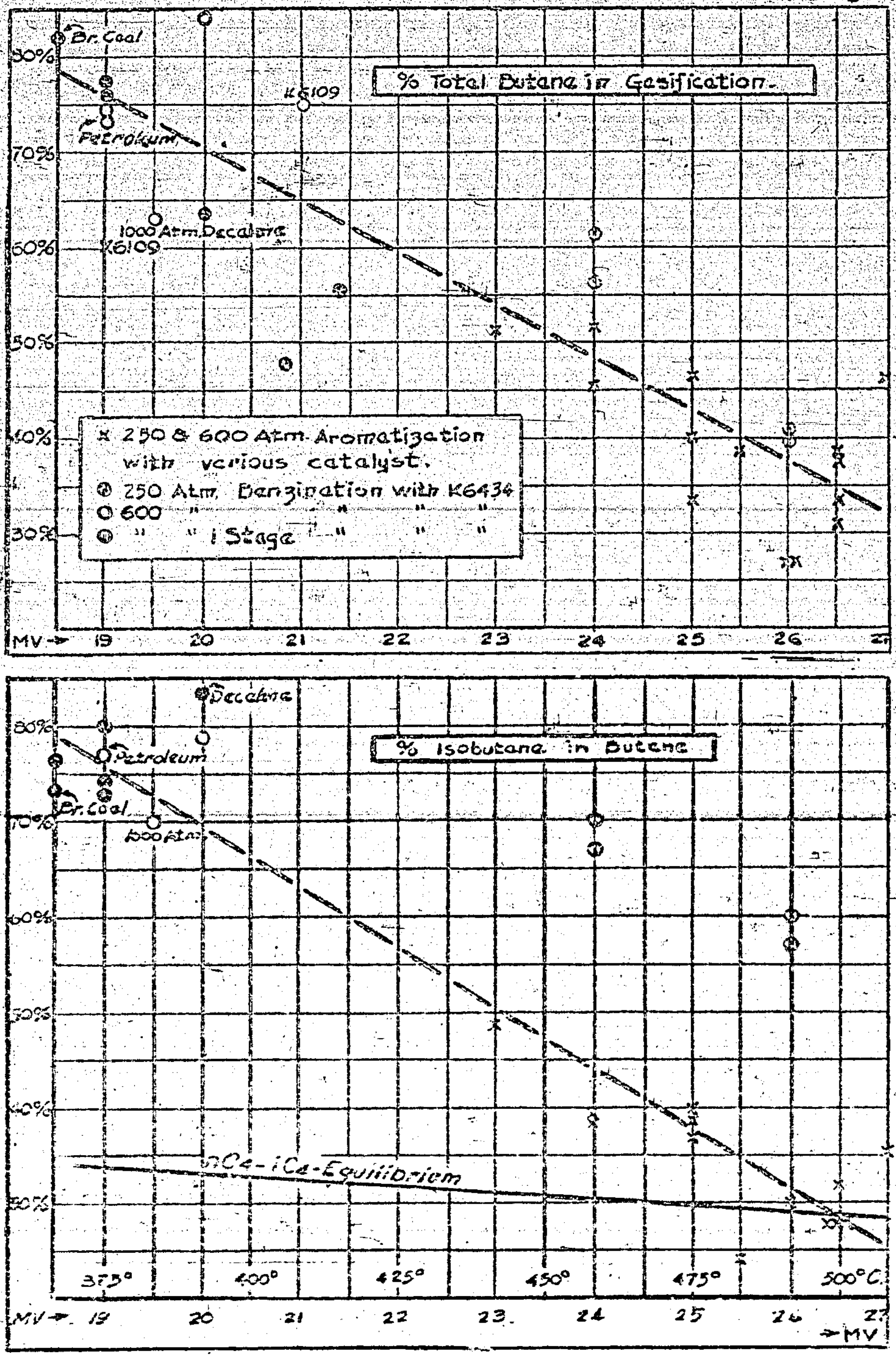
KCBraun
4-28-47

Butane and Iso-Butane Content of Gasification in Benzination and Aromatization With Fuller's Earth Catalysts (Experiments in 1 Liter Converter)

By Reitz, Ludwigshafen, 1 June 1943

Butane and iso-butane content of gasification in benzination with fuller's earth catalysts are primarily a function of the temperature and only very little dependent upon other conditions, such as active components of fuller's earth, 250 or 600 atm, starting material (feed), etc. The attached diagram shows values obtained in single-stage benzination @ 600 atm (mild aromatization), as well as in 250 and 600 atm aromatization of bituminous coal liquefaction middle oils and other pure oils, such as petroleum middle oil or decahydronaphthalene (decalene), at 200 to 250 and partly at 600 atm. The iso-butane content of gasification corresponds to the butane-isobutane equilibrium only at the highest aromatization temperatures (27-27 mV). At lower temperatures the isomerization equilibrium is not attained with the fuller's earth catalysts and the quantity of iso-butane produced by splitting is increasingly above the equilibrium value.

/fkp



SPLITTING WITH FULLERS EARTH CATALYSTS

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

676 T-309

KCBraun
4-8-47

Calorific Efficiency of Bituminous Coal Hydrogenation to Gasoline and Fuel Oil

By Dr. Wilde & Dipl. Ing. Schappert
Ludwigshafen, 7 March 1942
(See also T-139)

The production of aviation- and auto-gasoline in relation to heat consumption was investigated in "The Calorific Efficiency of Bituminous Coal Hydrogenation" (T-139).

It is clear that the production of fuel oil and gasoline (Silesian operating method) will give higher efficiencies, since the yield is greater and the H_2-consumption is lower.

But the greatest efficiency is obtained without the vapor phase, i.e. if the products of the liquid phase are considered the end products, gasoline, diesel oil and fuel oil, whose quality is to be subordinated in this investigation.

These two processes are based on the following specific figures:

		Liquid + Vapor Phase	Liquid Phase Alone
Coal Consumption	t/t	1.79	1.61
H_2-Consumption	m^3/t	2170	1600
Gasoline Production	t	0.464 (av. gas.)	0.20 (auto gas.)
Fuel Oil	t	0.536	0.48
Diesel Oil	t	--	0.32
L.F.G. (Liq. Fuel Gas)	t	0.171	0.098
Hy-Gas Excess	10^6kcal	3.2	2.4
L.T.C. Residue	t	0.229	0.205

On the basis of calculation of T-139, wherein only paste heat exchange was figured on from the start, the following calorific efficiencies are derived:

Liquid + Vapor Phase	Liquid Phase Alone
33.6	37.2

Analogous improvements may be made and consequent increase in calorific efficiency obtained here also:

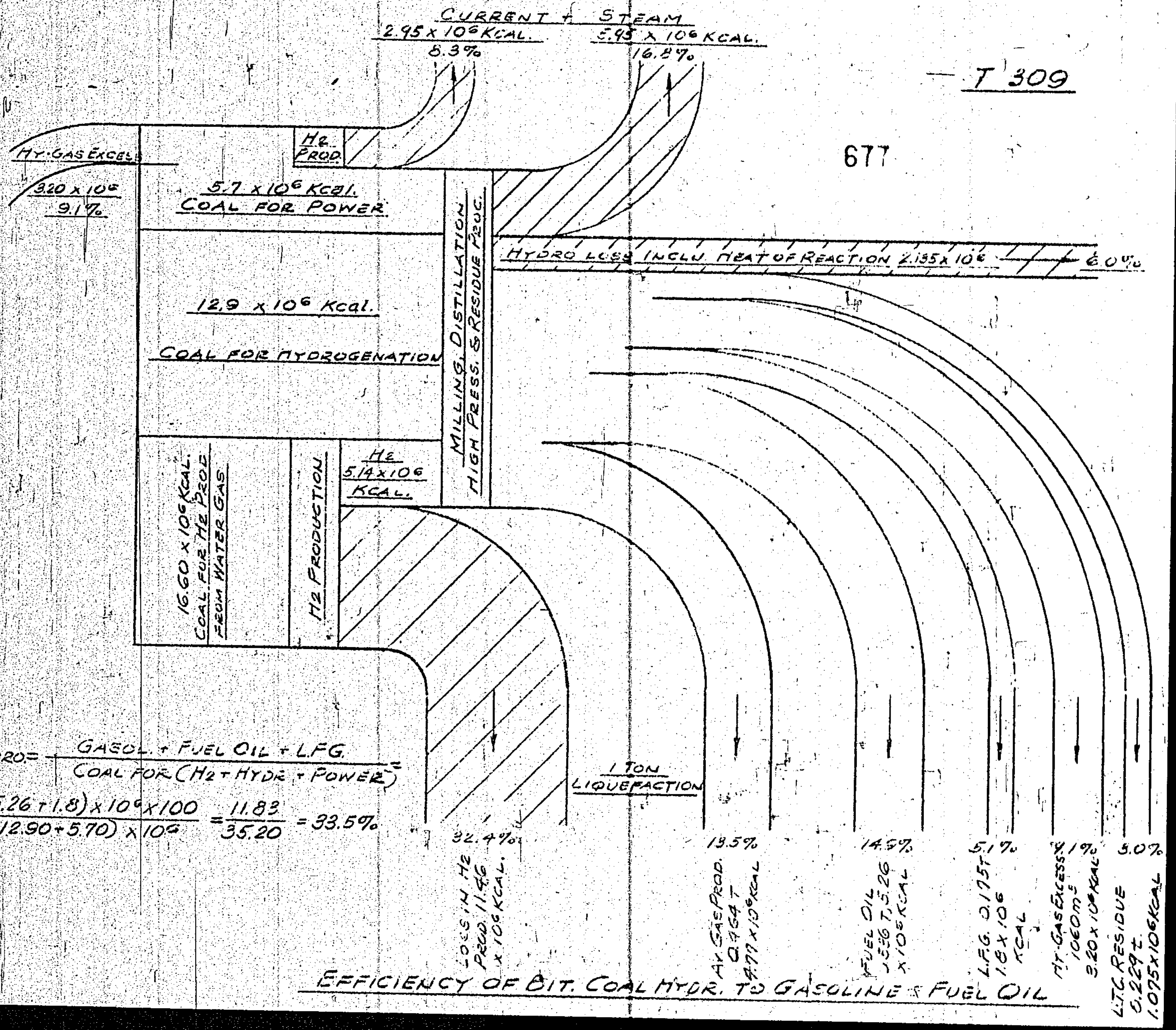
1) by the introduction of a Linde plant, in which the residual water gas and H_2 are decomposed, (E of H_2 = 39%), the efficiency rises to 39.2 and 42.6%

2) by utilizing the L.T.C. residue, the efficiency rises to 40.6 and 44.3%.

3) The live steam cooler for utilizing the waste heat in the letdown and product raises the efficiency further to 41.3 and 45.2%.

/fkp

T 309



$$E\text{-}HYDRO = \frac{GASOL + FUEL\ OIL + LFG}{COAL\ FOR\ (H_2 + HYDR + POWER)} = \frac{(4.77 + 5.26 + 1.8) \times 10^6 \times 100}{(16.60 + 12.90 + 5.70) \times 10^6} = \frac{11.83}{35.20} = 33.5\%$$

EFFICIENCY OF BIT. COAL HYDR. TO GASOLINE & FUEL OIL

Dr Miller

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

T-310

W.M.Sternberg
May 1947

TOM Reel 174m
frames 657-657a

Effects of Changes in Density upon the Flow of a Flowing Medium with a Horizontal Component of Motion

Ludwigshafen, October 25, 1944

Introduction

Changes in density are observed in most reactions in a liquid or gaseous medium, and are occasionally fairly extensive. If the reaction takes place in a horizontal tube, there may be produced, in addition to a horizontal progression, also a vertical component of motion, i.e. a layer formation of the heavier medium underneath the lighter, which may occasionally result in undesired effects, as shown in the example below taken from actual practice.

Example of Interference with the Course of a Reaction by Changes in Gas Density.

In tests on hydrocarbon synthesis from a CO-H_2 mixture, which need not be discussed in greater detail here, a type of converter of the following construction was tested: the catalyst was introduced into a vertical converter having the form of a vertical cylinder. The gas was supposed to flow from the inside of the cylinder radially to the outside (cf drawing at the bottom). The temperature of the catalyst could be measured at any point by means of a movable thermocouple.

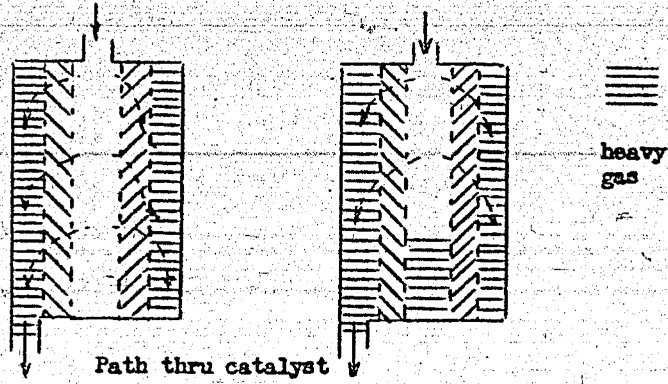
The surprising fact was found that no heat of reaction could be observed in the bottom part of the tube, while heat maxima were recorded at the top, which exceeded the permissible values. The principal part of the stream must have flowed through the upper part of the catalyst, while in the lower part practically no gas flowed through.

The explanation was found in an observation of the changes in density of the gas. The disappearance of most of the hydrogen and the formation of carbon dioxide and heavy hydrocarbons, caused the density of the gas to have nearly doubled, so that theoretically the gas outside the cylinder was twice as heavy as the gas inside. The results obtained were similar to what happens in a U tube, in one leg of which, in this case on the outside, a hydrostatic excess pressure was obtained which counteracted the drop in pressure, produced by the resistance of the gas flowing from the inside out. When this resistance to flow was less than the opposing hydrostatic pressure, and such was the case here, the heavy gas was forced to enter at the bottom from the outside. This disrupted however the whole distribution of the flow, no gas passed through the bottom of the catalyst cylinder, while too much passed through the top, causing the production of an unpermissible high temperature.

Application to Other Cases.

Changes in density are naturally the greater, the higher the pressure used. In the example above a pressure of 20 atm was applied. At higher pressures the effect would be much more strongly pronounced. However, even in this case the pressure difference would amount to fractions of an atmosphere, while otherwise the resistance to flow may amount to several atmospheres with a rapid flow (in the case cited above the flow was relatively slow); we must conclude from our reasoning, that in most cases changes in pressure would have no pronounced effect upon horizontal flow. However, whenever unexplainable phenomena are observed in converters, one must make tests to ascertain whether the phenomena are brought about by changes in density.

/fkp



Path thru catalyst

intended actual

FLOW

Signature illegible

C.H.

T-311 appears also on TOM Reel 250

680

T-311
W.M. Sternberg

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

High Pressure Experiments
Lu 558

March 27, 1943

M. Pier's Files.

HIGH PRESSURE VISCOSIMETERS

The need of a viscosimeter to measure the viscosity of paste under high pressure and at high temperature is repeatedly felt. As far as I know, there is as yet no solution of the problem. Primitive arrangements which have been repeatedly tested here, do not work.

An examination of the different methods of determination of viscosity appears to offer two which might permit to carry out determinations at high pressures. These are:

1). a process for the computation of viscosity based on the rate of a fall of a body

2). to use the moment of rotation produced by the liquid as means for determining viscosity

1) The first method is mostly used by measuring the rate of fall of a steel ball through the liquid to be tested.

Viscosity is determined by using Stokes' law

$$\eta = \frac{2}{9} \times 981\, r^2 \frac{\rho_K - \rho}{v} \times \left(1 + 2.4\, \frac{r}{R}\right)$$

where ρ_K and ρ are the densities of the material of the ball and of the liquid,

v -- rate of drop of the ball

r -- radius of the ball

R -- radius of the cylinder

The formula may be used only for a ball falling through the center of the cylinder. Uncontrollable deviations are avoided by placing the tube in an inclined position and permitting the ball to slide down the wall.

We could disregard this last refinement for measurements under high pressure, and keep the tube vertically. The sketch #3 shows how we believe the test should be run. The tube is either filled with the coal paste before the start of the test, hydrogen pressure applied, and heated; or else it is to be set up in the coal paste pipe line. The latter arrangement has the advantage of permitting measuring the inlet and outlet temperatures of the coal paste, avoiding the necessity of measuring the temperature inside the tube proper.

The ball is suspended by a sufficiently stiff steel wire to a small iron anchor, held in position with a small electromagnet (holding coil). When the current through the electromagnet is interrupted, the anchor falls off and the ball begins to sink. The moment of interruption of the current is marked on the stopwatch. The steel anchor fastened to the ball from above moves with the same velocity as the ball through a non-magnetic V_2A tube, which is equipped with standarized spools connected with condensers by voltage resonance, and causes the proper small lamps to light up when the anchor passes through the coils, which will permit to record the fall with a stop watch. One or two such indicator spools at the bottom end of the tube would be sufficient, and they will facilitate manipulations of the pull-up spool, which will be described below.

If the test is to be repeated, the ball will have to be brought back to the top. This is done by a special pull-up spool which is pushed by hand around the V_2A tube and again raised. The halting spool will in the meantime be again connected and will hold the anchor.

Advantages: made up of familiar elements, such as level indicating spools; no springs or other delicate parts in the high pressure space.

Disadvantages: no continuous recording.

2) The second method depends on transforming a moment of rotation through the liquid to some measuring substance was designed by Couette. The liquid is placed between two concentric cylinders, the outer cylinder being rotated at some angular velocity.

If M is the moment of rotation acting upon the inner cylinder, the viscosity is

$$\eta = \frac{M}{4\pi L \omega}\left(\frac{1}{R_1^{2}H} - \frac{1}{R_o^{2}}\right)$$

Sketches 1 and 2 show the way in which the process could be used in the high pressure installations. The outer cylinder is rotated by motor, the speed of which can be regulated, and which is located outside the high pressure space. The cylinder upon which the moment of rotation is transferred, hangs on a long rod, which is connected through a cooled tube to a suspension. The suspension (sketch 2) is suspended from a point in a way to permit it to rotate, and carries a contact arm which slides over an indicator (toroid winding). The opposing moment of rotation is supplied by a spiral spring. The spring and indicator are placed in a cold part of the high pressure apparatus. They are accessible after removing pressure resisting cap. The angle of rotation is limited to somewhat less than 180°, and provisions must be made for conversion to different ranges of measurements. This may be done without interrupting the test by changing the rpm of the driving motor. The continuous replacement of the paste in the rotating cylinder is done through holes in its bottom. The drain is located at the desired level. In this way, the level of the paste can never become too low, but may occasionally become too high, but can always be brought to the required height by throttling down the supply line.

Advantages: Continuous indications of viscosity.

Disadvantages: Complicated structure, use of delicate parts, such as spiral springs and electrical indicators.

/pkl

/s/ Hamacher

T-312

KCBraun
4-8-47

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

THE UTILIZATION OF COAL IN THE PRODUCTION AND USE OF DOMESTIC MOTOR FUELS.

By Dr. Kranepuhl, Berlin, 2. Feb. 1942
(see also T-138 and T-139)

The continuous constriction of the coal bottle neck leads us to examine the question, if a better utilization of coal could be obtained by changing the processes used in the domestic motor fuel production.

It is essential herewith that all essential factors contributing to the supply of motor fuels be taken into consideration. An evaluation of the processes with regard only to the efficiency based on coal consumption, without considering the quality of the final product, would not do justice to the processes currently used to produce high grade motor fuels and lead us astray in our planning, since the efficiency of coal naturally becomes poorer the more refined the final products are. The reason for that is, that considerable energy is required to produce the refined products, without increasing the heat value.

Every conversion of a process to another end product, possible in hydrogenation works, for example, entails a considerable change in the calculated efficiency. A comparison based on the efficiency at the motor shaft will also give a perverted picture. This measure of value would, in the first place, not satisfy the standards of value applicable to transportation, such as ton-mile for truck transportation or actual mileage for passenger traffic. In the second place, it would inadmissibly undervalue the quality calory, characterized by such properties as anti-knock, purity, volatility, anticorrosion, or willingness to ignite, demanded by motor transportation for the maintenance of its performance and particularly by the army to safeguard its technical superiority.

Motors are adjusted to quality. An airplane can not fly with a generator for solid fuels, not even with auto-gasoline, although the fuels in question are similar in nature.

In the third place, an evaluation based on efficiency neglects the difficulties encountered in the conversion and preparation of motor fuel power in the motor and is, therefore, misleading and practically inadequate. The motor fuel with the highest quality calory requires the least expenditure in equipment. Generator operation can not be compared with operation with liquid fuels or liquid gas; entirely different conditions with respect to useful load, motor performance, cost of maintenance, operating period, repairs, adaptability to traffic conditions, motor wear, range of operation, and difficulty in its supply. Therefore, only such processes may be compared as supply similar products of equal value, which can be used in motor transportation with the same expenditure in equipment.

Furthermore, in any comparison the equipment requirement of the individual process must be considered.

An arrangement, therefore, in the order of the coal efficiency or the efficiency at the motor shaft is only of theoretical value. Its practical application is limited to those cases in which an effect with respect to the coal consumption can be recognized, other conditions being comparable.

The following tables must be evaluated from these points of view. If our planning were based only on the efficiency, the steam engine, with a maximum efficiency of about 18%, would be our only basis of comparison and the future development built upon it.

The processes for the production of liquid or gaseous fuels can be compared from the most varied points of view, such as raw material requirement, iron requirement, space requirement, personnel requirement and others, all of which factors determine the price of the final product. However, the purpose of the final product will always be the determining factor in choosing the process.

In an arrangement of the processes according to their efficiency and a comparison of all fuels, it would be found that the less refined fuel had the highest use-factor. If we were to draw a conclusion from this fact and consider only processes with high calorific efficiencies, we would be taking a step backwards in civilization. The calorific efficiency can only be considered in a division according to the final product, although not primarily, but within the required limits.

Neither could the greatest efficiency be the determining factor in past planning, but primarily quality, iron requirement, utility, delivery time and the degree of technical development and safety of operations of the processes at hand. The army, navy and air force will always demand the best fuel with the best motor. The navy has been converted from coal to oil firing, in spite of the lower efficiency.

From the favorable efficiencies of many substitute fuels one would conclude that these should be used as much as possible. However, it should be noted that in many cases the planning to date has just provided the basis for the wider use of substitute fuels, so that the production of liquefied fuel gases in hydrogenation works today is greater than the combined production of motor fuels in Germany before the war.

The development of the generator is possible only after a suitable fuel becomes available, because the German wood supply is inadequate. The L.T.C. coke produced in the bituminous coal low temperature carbonization program will clear the way for this.

We must, therefore, stick to the idea that, while for comparable processes the coal efficiency or the efficiency at the motor shaft may indicate the choice of the process, these efficiencies must not be misused for a general grading of the processes in such a way that conversions in the entire motor industry will become necessary, the effects of which can not be determined figuratively in a manner similar to the efficiencies. Such conversions have certain disadvantages, which eventually cause increased material consumption and increased coal requirements, while there is no relation between these disadvantages and the saving in coal, because only 3.5% of bituminous coal consumption and 14% of brown coal consumption was used for mineral oil production in 1941. These percentages will rise to 5.5% for bituminous coal and 17% for brown coal in 1942. Even a saving of 30% in this direction would mean only about 2% bituminous and/or brown coal injection, by which Germany's entire motorization would be endangered, while other consumers with 25 to 30% of the total consumption offer much greater possibilities for saving, such as electric power production from 30 million tons of middlings in bituminous coal mining (ballast coal), which now remain in the ground, and from which 11,000,000,000 Kwh/ann. could be produced. The utilization of this source of energy has so far been neglected only because RWE (Rheinish-Westphälische Elektrizitätswerke) does not want the coal mining industry to participate in public utility power production, according to the Ruhr coal mining industry.

The tables (not available, but compare T-138) divide the individual processes into 5 groups:

Table I:	High pressure hydrogenation and synthesis processes.
Table II:	Combined hydrogenation and synthesis processes.
Table III:	Processes for the production of bottle gas at 250 atm.
Table IV:	Motor fuel processes for use in vehicle generator.
Table V:	Comparison with other means of transportation.

1). Table I shows that, based on the calorific efficiency of bituminous and brown coal, which ranges between 36 and 40%, depending upon the products produced, high pressure hydrogenation and Fischer synthesis are about equal. The efficiency of power production at the motor shaft is between 9 and 10%, based on coal consumption. Bituminous coal hydrogenation is used primarily for the production of high performance aviation gasoline and lately also for marine fuel oil, and brown coal hydrogenation for the production of 87 octane aviation gasoline, auto gasoline and diesel oil. The Fischer synthesis is used primarily to cover our requirements of diesel oil and paraffin.

2). Table II shows the combined processes of low temperature carbonization and/or coking of bituminous and brown coal with subsequent tar hydrogenation and L.T.C. coke synthesis. The efficiency of bituminous and brown coal carbonization may be calculated in various ways. The losses occurring in carbonization can be changed entirely either against the excess coke or the liqued fuels, depending upon whether carbonization is intended primarily for the production of coke or of motor fuel. For bituminous coal carbonization with subsequent tar hydrogenation (compare case I) we then get an efficiency between 37 and 59%, depending upon the method of calculation, and for brown coal carbonization with subsequent tar hydrogenation (compare case II) between 44 and 60%. Table II was compiled so that the losses in carbonization were credited partly to coke and partly to tar, depending upon the calory content.

Table II also shows that, even though the coal consumption, i.e. the quantity of coal directly converted into motor fuel, is comparatively low, the coal requirement, particularly in bituminous coal carbonization, is many times as great. The difference between coal consumption and coal requirement gives us a rough idea of the quantity of by-products obtained. All of the combinations mentioned in this table are used in Germany today.

Since in combined brown coal carbonization and tar hydrogenation the excess of Grude-coke is relatively small compared to bituminous coal carbonization, and since the problem of the disposal of the excess Grude has recently been eliminated by its use in power plants, the combined process of brown coal carbonization and hydrogenation could be carried out to its fullest extent. Brown coal tar gasoline quality is near the lower limit of aviation gasoline requirements, although the auto gasoline and diesel oil produced by this combined process is qualitatively very good.

Bituminous coal carbonization could just recently be carried out in earnest, because the process was not sufficiently developed for large scale production and the market for excess coke, as well as its use, was not sufficiently clarified. The process combination of bituminous coal carbonization and bituminous coal L.T.C. coke produced for the production of H_2, is presently being built in Upper Silesia.

It is obvious that synthesis may be coupled to carbonization and subsequent tar hydrogenation (compare items 3 and 4 of Table II). In the necessary production of the various products obtained in hydrogenation and/or subsequent synthesis, care must be taken that they be in accord with the demands for aviation and auto gasolines, diesel oil and paraffin. Item 5 shows a process combination in which bituminous coal carbonization is replaced by bituminous coal coking. Such a combination is used in several plants in the Ruhr. The point of view of scarcity of good coking coal in the Ruhr district and in Upper Silesia is opposed by a wider demand. The use of the bottle gas produced in this combination at 250 atm is further explained below.

3.) Table III. Gases with a heating value of 4250 kcal/m^3 are produced in this process as motor fuel. These are bottled at 250 atm, and can also be used in motor transportation, if need be. Bottle gas is particularly suitable for the operation of stationary engines under favorable conditions. Its disadvantages for motor transportation are its small radius of action of about 300 km and the heavy bottles, which reduce the pay load of a 5 t truck by 3 tons.

4.) Table IV shows those processes which supply fuel for vehicle generators. The vehicle generator can not replace the motors required for war vehicles, which must be operated with liquid fuels. Even in the future, its use will be of importance only for heavy trucks and busses.

The gas plant that must be carried along is heavy, requires special servicing and takes up much space, since a cooler and a cleaner go with it. The conversion to generator gas is coupled with an appreciable loss in motor capacity and the gas production is difficult to adapt to the varying demands of practical vehicle operation.

For this reason and also because of frequent repairs to the generator equipment, good economic results can only be achieved when properly trained operators are employed in servicing the vehicle. It is interesting to know in this connection, that no savings in iron requirement can be obtained with generator operation, as the following calculation shows:

> 10000 generators require 50000 t iron. 10000 diesel trucks of equal pay load capacity require 80000 t of diesel oil per annum for the production of which 50000 t of iron are likewise required.

5.) For comparison, Table V shows the efficiencies of the steam locomotive and the powdered coal motor. If the application of a certain process were determined by its calorific efficiency alone, this would favor the steam locomotive, because its efficiency at the motor shaft equals 70%, based on coal consumption. However, the demand for non-rail transportation with a wide radius of action can only be met by Otto and Diesel engines.

In order to satisfy transportation requirements, we must consider many demands which, in turn, must be suited to the latest degree of technical development. Economic considerations, however, take first place.

TOM Reel 9, pp 270-287

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

T-313

THREE PAPERS ON GAS HYDRATES

I

High Pressure Experiments
Lu 558

December 4, 1941

Report on Discussions of Dec. 4, 1947 in
Ludwigshafen/Rhein

I. Report from Pölitz on the shut-down of a coal stall. Information on similar occurrences at other plants, in particular about plugging up through the formation of gas hydrates, ammonium carbonate, etc. Technical precautions to avoid gas hydrates.

II. Literature on gas hydrates. (Translated by Dr. Kandiner, Bureau of Mines, Pittsburgh, listed in Louisiana Coal Hydrogenation Plant file as T-316.

III. Control of the pressure differences produced during the plugging. Translation T-73, Bureau of Mines.

IV. Discussion of other experience during disruption of operations in high pressure stalls (emergency HOLD, bursts of flame, connections between converters).

I...Dr. Wissel reports about a shut-down of the coal stalls 13 and 15 in Pölitz.

There are four coal stalls in Pölitz, in groups of two on one circuit. The pressure difference in the circuit amounted to 60 atm. The pressure difference per coal stall amounted to 30 atm. On the pressure side, the gas circuit is supplied to the stalls in two bundles, separate from the gas circuit of the tar stalls; on the suction side the gas of the tar stalls is no longer carried separately, and there are therefore three parallel bundles. The make-up hydrogen is added to the circulation pumps on the pressure side.

About 8 days before the day of the accident a strong retrenchment of operations became necessary because of formation of ice slush in the canal. No difficulties were experienced on the day of the accident. The gas supply and the total cold gas suddenly became reduced in stalls 13 and 15 at 11 o'clock. The intake gas passing through the stalls amounted to 25,000 m^3, with 30,000 m^3 of cold gas passing through one stall, and somewhat less through the other one. All the first precautions taken, such as opening up the valves of the make-up gas and cold gas inlets, were of no avail. The operations were immediately changed over to pasting oil; the circulation gas pressure difference was increased. Pölitz was able to operate on 100 atm. pressure difference, when it normally was kept at 60 atm. The temperature in the converters rose in the next six minutes from 27.2 to 27.8 mv. The changing over to pasting oil in the first converter has worked successfully, but it has not been sufficient to lower the temperature. About six minutes later the gas suddenly began again to pass by, the stalls were passed by, 2 - 3 minutes later a pipe between the 2nd and 3rd converters burst, ½ minute later the pipe line between the third and fourth converters in the second stall. The emergency let-down was put in operation, but the going through could not be prevented.

Investigations made have shown that the sudden stoppage of the gas by passing was caused by hydrocarbon hydrates. During the pressure release in the stalls on the next day, pieces of gas hydrates were found. After all excess pressure has been released, gas analysis proved the presence of hydrocarbon gases, which had to be explained by the existence of gas hydrates. A few days after the trouble, gas hydrates were blown out. The Pölitz circuit is operated with water injection. The water is separated from the circuit behind the oil scrubbers.

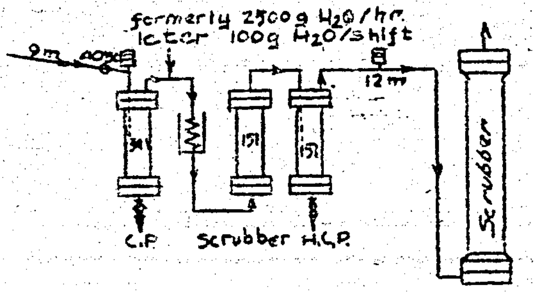
It is particularly to be regretted, that in the adjoining stall 14, where men were working, two fitters received mortal wounds. Provisions were made to give warning signals to men working in a stall next to one where there are difficulties.

In conclusion, photographs were shown of the two damaged stalls.

Dr. Pier: An official description of the accident has been sent to all the participants of the meeting. The first explanation one could think of was the plugging up of the gas circuit with gas hydrates. The presence of gas hydrates has actually been proven.

Dr. Pier next suggested, that representatives of the different works discuss their experience with gas hydrates. It was equally important to discuss the removal of ammonia and the formation of ammonium carbonate. It is known, that above a certain temperature, 35 - 40° C, gas hydrates are no longer stable, regardless of the water and hydrocarbon concentration. It is known from the literature and from the American oil industrial experience, that the different gas hydrates mutually affect each other. The presence of ammonia, oil or alcohol reduces the danger of formation of gas hydrates. The formation of gas hydrates is also prevented by the presence of very large amounts of water. It is however practical to use as little water as possible. As the temperature is raised, the concentration of steam is increased in the circuit, and with it also its partial pressure. Should cooling take place anywhere in the circuit, steam will condense, which will produce conditions favorable to the formation of gas hydrates.

Dr. Simon told of the difficulties experienced in the large and small scale equipment in Ludwigshafen through the formation of propane hydrate. The first trouble attributed to propane hydrate occurred in June 1938 in a 100 li. converter. The converter was operated at 700 atm. pressure with cracking residues, the amount of circulation gas was 185 m^3/hr. The circulation gas contained less than 18% hydrocarbons, the average carbon number was 1.4. A pressure difference became established, and could not at first be located. It was assumed, that the trouble was to be attributed to the presence of ammonium salts, and the water flushing behind the catchpot and the heat exchanger were increased to 1.5 kg/hr of water behind the heat exchanger and 2.5 kg/hr behind the catchpot. These precautions were not however sufficient. The converter had to be cooled and turned off. Testing the equipment did not help in locating the plugged up place. On thinking the matter over it was assumed that the trouble was caused by gas hydrates. Immediately upon starting again pressure differences reappeared. The pressure difference disappeared every time the pressure was reduced from 700 to 200 atm. This pointed definitely



Outlet of Converter 703. Working up of cracking residues.

to the presence of gas hydrates. The normally connected piston differential manometer permitted only measuring the pressure differences between the catchpot and the outlet pipe line behind the water scrubber. This pipe line has therefore been heated, and the water flushing behind the catchpot was reduced from 2.5 kg/hr to 100 g/ layer. The pressure differences then disappeared.

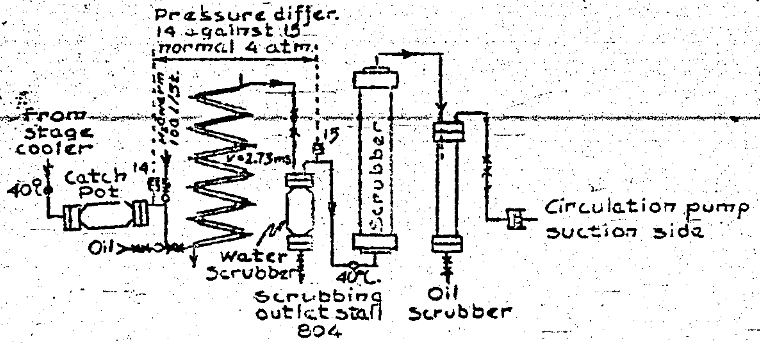
Two precautions were taken to prevent such trouble:

1) The whole pipe line was heated to 40° C; and

2) the water injection was reduced as far as possible.

A second case of formation of gas hydrates was observed in the large scale experiment with fuel oil in the 700 atm. stall 804, in September 1941.

To avoid the formation of gas hydrates, the pipe lines from the catchpot to the intake into the oil scrubber were heated to 40°; in addition , 100 li/hr of warm water was injected behind the catchpot to prevent the formation of ammonium carbonate.



During the operation of the stall (large scale fuel oil test) a pressure difference of 4 atm. usually existed between the outlet from the catchpot and the intake to the oil scrubber. The oil scrubber itself produced no noticeable pressure difference. This pressure difference prevailed in the whole stall outlet during the whole 10 week test, with a single exception, when the stall difference rose from about 23 to about 29 atm. The gas intake gauges showed irregularities, and there existed the danger that the gas intake could no longer be maintained. The stall was changed over to pasting oil. Tests have shown, the pressure difference to have existed in the pipe line between the catchpot and the oil scrubber. This piece of pipe became cold because of the failure of a condensation trap. When this trouble was eliminated, the pressure difference returned to its normal value and regular operations could be resumed. 4350 m^3/hr of gas was used in the circuit. The circulation gas had the following composition:

10% methane

2% ethane

1% propane

0.5% butane.

A third case of formation of propane hydrate was observed in the DHD stall while the converter was being filled with the pressure release gas. The outside temperature was very low, and the operations were carried out at 50 atm.

Dr. K. Winkler told of troubles with propane hydrate in Welhem. The circulation gas was not heated when the liquid phase was started with 650 atm. in the fall of 1937. Water was injected into the gas cooler and into the circulation gas to avoid pluggings up with ammonium carbonate. Shortly after the start, with the outside temperature not exceptionally low, propane hydrate began to form in the 70 mm pipe line of the ciruit. Propane hydrate rods could be pulled out of the pipe line. Since then, the whole circuit is heated to 35 - 40° C, and no more water injected into the circuit. Care is taken to have no liquid water in the circuit, under the assumption, that gas hydrates are only formed, when liquid water is present. No more difficulties with propane hydrate have been encountered after these precautions have been taken.

Welheim now avoids the formation of ammonium carbonate by adding no carbon dioxide to the circuit, only ammonia. To do this, the CO_2-containing make-up gas is added shortly before the compression of the circuit, and all CO_2 is scrubbed out in front of the catchpot.

A second case of difficulties from gas hydrates occurred in December 1940 in the vapor phase. The operations in Welheim are carried on with a relatively dense gas (0.340 - 0.450) and without oil scrubbing. The H_2 concentration is around 53 - 55%, the pressure 650 atm. The gas cooler is connected twice in parallel. We explained the trouble by assuming that the flow became stopped through one of the systems of the cooler, and that the pipe lines became cold. The propane hydrate crystals grew in the pipes. It could be eliminated by passing steam through the pipe line.

A third case was met in the end of Dec. 1940 - beginning of Jan 1941, with a newly installed coal stall; the stall was filled up for the first time with the circulation gas. Because of scarcity of gas, the stall was filled with circulation gas instead of hydrogen. There existed all conditions favoring the formation of propane hydrate. The pressure difference in the stall rose suddenly from 3 to 41 atm. In the heat exchangers, the converter pipe line, - propane hydrate crystals were found everywhere, deposited from the hydrocarbons of the gaseous mixture and the water of the insulation. It took some 14 days to thaw out the pipe lines. The rule has since then adhered to of not filling a new, still moist stall with circulation gas.

In the United States, hydrocarbons are thoroughly dewatered, even though it is costly.

Dr. Frese added on to Dr. Winkler remarks from records, in which the events were summarized.

Dr. Kuppinger reported of trouble in Leuna vapor phase caused by gas hydrates during 1936 while operating with 5058 in the prehydrogenation. The same phenomena were met with in Bari in 1938 during prehydrogenation, and in an aggravated way. Gas hydrates formed in both cases in the suction side of the circulation gas pipe line, while the load on the stall was still small, and much gaseous hydrocarbons were formed. They could be avoided by suspending the water injection into the heat exchanger.

Dr. Urban: The formation of gas hydrates has never been observed in Scholven. Conditions with 300 atm. are more favorable for the avoiding of formation of gas hydrates, than at 700 atm. There was trouble in Scholven in the gas coolers in front of the oil scrubbers connected in parallel, but that had to be attributed to ammonium carbonate. At present the rule is being enforced of having a man touch the coolers every 15 minutes to see whether they are too cold.

Level indicators and all measurement pipe lines are continuously heated in Scholven. The catchpot products are kept at 55-65° by throttling the cooler for the products, to prevent the formation of a foam phase.

The circuit is neither heated nor even insulated. However, being the first coal hydrogenating plant, Scholven has only short circuits (100 - 150 m), while today the different building are set as far apart from each other as possible. The stalls in Scholven are located closely together with a relatively hot circuit pump installation. The circuit is rather well protected between the buildings.

About 800 li of water/hr/stall is injected into the coal phase stall and the same amount into the vapor phase. Scholven must inject water into the circuit, because otherwise ammonium salts are not sufficiently well eliminated. The make-up gas is added in front of the suction.

Nor have any gas hydrates so far been observed in Scholven in the vapor phase. Because of insufficient cooling, the catchpot temperature is 25 - 30°. The reflux cooler designed for only two stalls, is insufficient for four.

Dr. Urban has made the further remark that plugging up has frequently occurred in the large-scale installation stall 803 in Ludwigshafen in the parallel tubes of the cooler.

Dr. Jacob reported about the troubles in Gelsenberg. Gelsenberg has been started two years ago. Until no water was injected into the stalls, troubles were met in the water cooler, which could be overcome by injection of water. The formation of ammonium carbonate has been proven.

In November 1939, the only stall then in operation was receiving no cold gas. The stall was then immediately let down. After the emergency let down, the stall was again filled with gas. The circulation gas pipe line was taken apart, but neither ammonium carbonate nor propane hydrate crystals were found in it. Troubles have also occurred in washers, caused by pressure differences. Investigation has shown, that the Raschig rings were completely pressed together. Neither ammonium carbonate nor propane hydrate was found here either. It may be that propane hydrate had formed immediately in front of the washer, and then been passed through.

Nothing of this kind has occurred in the vapor phase.

For some time now, no circulation disturbances have been met, possibly because the gas coolers are operated in a way to keep the temperature of the washing installation at 30 - 35°. The products leave the catchpot at a temperature of close to 60°, and are cooled in the gas cooler to 35°. The pipe line between the catchpot and the circuit is heated. Similarly, side lines and by passes of the circuit are heated. Gelsenberg injects 500 li water per hour per stall into the circuit, 1000 li/hr are injected in front of the stall cooler. At the stall outlet and on the inlet side to the circulation gas there is 0.05% ammonia and 2.1% CO_2, i.e. the carbon dioxide is in excess.

Dr. Roser reports of a case in Zeitz in the fall of 1940. A reserve stall for TTH was repaired at below freezing temperature. When later filled with gas, (16,000 m^3 of gas passing through), there was a large pressure difference. The pressure difference could be lowered in the course of a few hours, but not entirely overcome, and the stall was re-opened. The elbows at the inlet of converter 2 had a strong constriction in the cross section. The plug consisted of a snow-like mass, which, after melting, produced a large amount of gas. The gas was tested and had the following composition:

20% H_2S

23% CH_4

4.7% C_2H_6

27% C_3H_8

20% C_4H_{10}

3.7% higher hydrocarbons.

No water had been injected. The temperature of the circuit was 30°. No other difficulties have been encountered in operation.

Dr. Peukert: The gas circuit in Rheinbraun has 8 parallel bundles in the cooler. The pressure is 500 atm., 15% hydrocarbons in the circulation gas; C number 1.3. Because of foaming, the catchpot must be operated very warm, i.e. at 70°. 1000 kg water/hour are injected into the stall. The circulation gas is saturated with water behind the catchpot. The gas is cooled to 25° in the circulation gas cooler. It was found one day, that no gas was passing through some of the eight bundles of the gas cooler. Water was added in the plugged up spots, and steam introduced. This freed again all the bundles. Since then the cooler outlet temperature is kept at 30°, and no more plugging has occurred. There are but a few milligram of ammonia in the circulation gas, the carbon dioxide content is 2 - 3%.

In the vapor phase at 300 atm. no troubles have been experienced.

Dr. Hahn reports of trouble in the level indicators. These were overcome by heating the pipe line, and using make-up gas as the flushing gas.

Dr. Schmitt: During the cold part near the end of January 1941 the pressure difference in the product cooler rose suddenly in the 6434 stall, which was operated with a small load. The increased pressure difference was not, however, sufficient to necessitate the closing down of the stall. Sometime later, the stall had to be closed down because of feed shortage, which permitted to examine the stall and disclosed the existence of gas hydrates. The gas hydrates were formed with a gas pressure of 300 atm., and at a temperature of 15°. The water injection amounted to 500 li/hr into the last heat exchanger, 1000 li/hr behind the product cooler and 500 li/hr per stall into the circulation. This large amount of water injection is done to keep the ammonia content at 1 - 2 mg/m^3.

In the tar liquid phase a plugging up occurred, probably near the circulation gas cooler during operations with producer tar at 700 atm. The catchpot temperature was 30-35°. The gas passage was reopened by reducing the pressure. It was decided that it had been caused by the formation of gas hydrates. The catchpot was then operated at 50 - 60°, and no more plugging has been observed.

II. Dr. Nonnemacher gives a survey of literature on gas hydrates. His report has been translated by Dr. Kandiner of Pittsburgh, from reel 9, pages 288 - 296. (T-316)

III. Schappert reports on the gas circuit at 700 atm, particularly from the viewpoint of the measuring technique. Translated - Bureau of Mines - T-73.

Dr. Drucker. Scholven measures the pressure difference of the whole stall, the pressure difference of the oil scrubbing including the circulation gas cooling, where gas hydrates may form. A by-pass around the oil scrubbing may be put rapidly in use with the help of certain valves, should any disturbances be experienced. These valves are in a small space of about 2 m^2, permitting their being used in but a few seconds even by hand. Heating is provided for this small area and easily done.

There are no electrical valves on the coal side in Scholven, only oil operated valves. Oil operated valves have been proven to be more satisfactory on the coal side.

Dr. Küppinger showed a schematic presentation of the Leuna circuit. The total length of the circuit is about 1200 m. Pressure 250 atm. The pressure differences are measured with the ordinary manometers of the firm Eckardt. The pressure difference in Leuna amounts to only 27 - 28 atm. There is a dial manometer in each stall. These manometers indicate sufficiently accurately at 250 atm, other measurements are not provided for. In Leuna, instead of measuring the amounts in the parallel lines, as suggested by Mr. Schappert, measurement is made in the circulation gas by-pass. Mr. Schappert expressed the suspicion, that such measurements would be subjected to great fluctuations, while the proposed method of measurement in the parallel bundles would be sufficiently buffered.

Brabag: In Brabag the measurements are essentially the same as in Leuna. The pressure difference in the circulation gas is measured in the Leuna way.

Dr. Frese: In Welheim the pressure difference in the circulation gas is measured in duplicate. There are two recording air activated manometers in Leuna. However, these manometers are frequently very slow. They give rapid readings at the normal pressure difference, but with a difference of 50 atm., it takes the manometer 2 - 3 minutes to reach the final indication.

Mr. Egli tells about the slowness of recording by air operated manometers. Systematic measurements have shown that with larger pressure differences it takes 2 - 4 minutes to reach the final reading, while the in the cylindrical differential manometers leg amounts to only a few seconds. Mr. Egli suggests therefore that in the most important parts of the circulation gas differential pressure connections should be provided for an air activated and a piston differential manometer.

In service the air actuated manometer is easier to use. The operator is however in position to notice abnormal pressure indications on the piston manometer. Gelsenberg doubts whether the service man on the maintenance of the pressure difference should be permitted to raise the pressure difference of the circulation pumps in case of trouble. The opinion has been reached, that independent changes of the circulation pump pressure difference by the attendant may produce more harm than good.

IV. Should gas be passing thru, the emergency let-down is immediately used. The first converter in each stall is let down first, than the second, third and fourth.

Dr. Winkler and Dr. Frese. In Welheim the first converter is also let down first. There are no electrically operated valves in

Welheim. The valves must be operated by hand. Two valves must be opened for the emergency let down of the first converter. Converters 2, 3 and 4 are then let-down.

Dr. Urban. Whenever there is a temperature rise, Scholven uses the emergency let-down. All the converters are let down simultaneously. In most cases one may again operate with the full amount of paste in 6 hours.

Dr. Pier suggested in view of the Pölitz accident, that waste burners be provided in the stalls. He called attention to the experience that the gas becomes ignited in most cases when gas escapes or a combustible liquid is present. This resulted in a lively discussion, in which

Dr. K. Winkler mentioned, that the higher the pressure, the more readily gases ignite. In one particular case the escaping gases from a 700 atm. stall in Leuna ignited too late. The detonation of the mixture cloud had a very extended spread.

Dr. Pier: The pictures shown by Dr. Wissel show, that consideration should be given to the vertical pipe lines in a stall being strengthened, or else that the connections between converters be made as short as possible. Vertical pieces should be avoided as far as possible.

Ing. Berger sketched a suggestion in which the long hot connection lines would be avoided by placing the riser tubes inside the converters and joining them together. The length of the connecting lines would then amount to only 45 (?) of the present risers.

From constructional considerations the execution is readily possible. In such a case, particular attention should be paid to heat expansion of the hot connecting lines.

To avoid coking, the dipping tube should be led downwards along the edge of the converter, as is done in the hot catchpot.

The suggestion has also been made to deliberately weaken the piece of piping leaving the converter, in order to create a sort of a "shear pin" in case of the converter passing through.

A weakening of that kind is possible and practical, if the upper sector of the tube (half the circumference) is eroded down to limiting wall thickness for a distance of 1 meter.

From Dr. Pier's private files. 699

Ruhröl G.m.b.H.
Hugo Stinnes Werke

Bottrop

High Pressure Experiments
Jan. 14, 1942. Be/Le
P/Lu 558

DISCUSSIONS IN LUDWIGSHAFEN, DEC. 4, 1941.

We informed you in our letter of 12/15/41 briefly of the meeting on 12/4/41 devoted to the prevention of plugging (especially by gas hydrates). We add now in the appendix the report of the discussions.

We will attempt to find the theoretical basis for the formation of gas hydrates from hydrocarbon mixtures, and repeat our request to make available to us the necessary data for the calculation of equilibria. We will need for this purpose information on the connection diagram of the gas circuit, the operating conditions, the amounts of gas, temperature, composition of the gas at the principal places (including the make-up gas), and also the amounts of water and oil injection. These data are required for the formation of gas hydrates as well as for normal operations. To make it easier for you, we add a questionaire.

That part of the discussion which referred to construction of the stall walls will be transmitted to you in a special report, together with the conclusions drawn from it.

We wish to take this opportunity to request all the different works to inform us, as a form of exchange of experience, of all the important disruptions and special events, as well as precautions taken to overcome the difficulties, which may be important for the other hydrogenation plants as well as for new designs, and may contribute to the avoidance of troubles and accidents there.

/s/ V.Simon....Kleber.

III

HYDRIERWERKE PÖLITZ A.G.

I.G. Farbenindustrie A.G.
Div. of High Pressure Experiments

Stettin - Pölitz
2/18/42.

Re: Gas Hydrates.

In reply to yours of 1/14/42 we are sending you the operating conditions in the vapor and liquid phase as requested in your questionaire for the different cases of formation or prevention of gas hydrates.

We mention about the three cases of formation of gas hydrates at our plant, and that the means to prevent their recurrence;

1. The catchpot temperature in the liquid phase is always kept above 60° C.

2. The liquid phase circuit is heated and insulated on the pressure as well as the suction side,

3. The stage coolers in the vapor phase are provided with warm water return, so that during cold weather the cooling water can always be kept at a temperature around 10°.

2 illegible signatures.

IV. On the Formation of Gas Hydrates.

Pölitz, 2/14/42

We may mention with reference to the plugging up with propane hydrate on 11/25/40, that the gas hydrate was formed in the circulation cooler, when the catchpot temperature (W thermocouple) was not operated at the usual temperature for coal products at 70°, but was kept at 30 - 35°.

The gas hydrate formation which has caused the explosion of stalls 13 and 15 on 11/21/41 was caused by the failure of the water supply (which resulted from the formation of ice mush in the intake), and with the interruption of power and steam production caused by it. The catchpot temperature was temporarily raised 100° but the long circuit III cooled nevertheless because of the strong cooling.

The gas hydrate formation on 1/28/41 took place in the product cooler. The temperature of the catch pot shown, 35°, should not mislead, because it indicates a secondary phenomenon. The W thermocouple had indicated a temporary temperature of 10° because of the strong cooling. The resulting formation of propane hydrate plugged up the cooler down to 2 bundles, which were forced to handle the cooling of the whole production. The high load on these two bundles in the cooler has resulted in the temperature of the W couple rising to 33° in spite of the completely suspended water supply.

/s/ Köcher
Ehrke

W. M. Sternberg.

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Hydrogenation Works Pölitz A.G. **Copy** T-313

Liquid Phase

Stall No.	1/15 1942 No (hydrate formation 11	12	13	15	11/20 1940 Hydrate format. Stall 11	11/21/41 Hydr. format. Circul. Plugg. up stalls 13 and 15.
Press. circul. pump pressure side	708	708	708	708	707	704) (I) 705 (II) 704 (III)
Press. Circul. Pump suction side	649	649	649	649	650	650 645 645
Pressure where hydrate was formed					665	abt. 655
l/h water to Product cooler	1,300	1,300	1,300	1,300	500	ca. 1,000
l/h water to heat exchange.	500	500	500	500	500	ca. 800
l/h water to circuit	200	200	300	300	500	ca. 500
Catchpot with no water	12	16	16	16	10	17 to/hr
Temper. in catchpot	70°	70°	75°	70°	30 - 35°	70°
Outlet gas, all stalls	160,000				35,000 (11)	130,000 (11, 12, 13, 15) m³/hr
Temp. circ. gas, press side	Circuit I 59°		II 59°	III	56°	56°
Temp. circul. gas, suction side	48°		48°	Tempor.	38°	37° (I, II, III)
Temp. gas cooler	36		35°	not in	abt15°	35° (I) 38° (II) 7° (III)
Temp behind gas cooler	32°		33°	use	abt15	abt. 30°
Make-up gas, m³/hr	49,000				10,000	0,000 (coal stall abt. 25,000)
Addition to circuit	In 1. and 2 pressure side				1. press. side	1. and 3. Press. side
Am't scrubb. Oil x) m³/h	70				Oil scrubber not yet in operation	100
Temp. of scrub. Oil	35°					30°

	Pressure side 1 & 2	Suction side 1	Suction side 2	Presc.	Suct.	Pressure 2 and 3	Suct. sd. I	Suct. sd. III
CO_2	0.1	1.0	1.4	0.0	0.0	0.1	0.2	0.3
H_2S	0.0	0.2	0.5	0.0	0.0	0.0	0.1	0.1
O_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H_2	87.9	76.0	76.7	86.4	85.6	82.3	75.0	78.1
CO	1.1	0.5	0.5	0.0	0.0	0.9	1.7	0.9
N_2	1.2	6.9	7.4	8.4	8.6	6.2	7.0	8.0
Hydroc.	9.7	13.9	13.1	5.2	5.8	7.7	15.3	14.6
C No.	1.42	1.35	1.44	1.19	1.31	1.37	1.37	1.32
C_nH_m	0.0	0.4	0.3	0.0	0.0	0.0	0.0	0.0
NH_3 g/m³		0.007	0.007	—	0.078	0.01	0.02	0.025

Composition of Make-up Gas			
H_2	96.8	97.0	97.1
Hydrocarb.	0.6	0.6	0.4
C-No.	1.00	1.00	1.0
N_2	2.6	2.4	2.5

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x) No vacuum installation available.

Hydrogenation Works Pölitz A.G. **Copy** T-313

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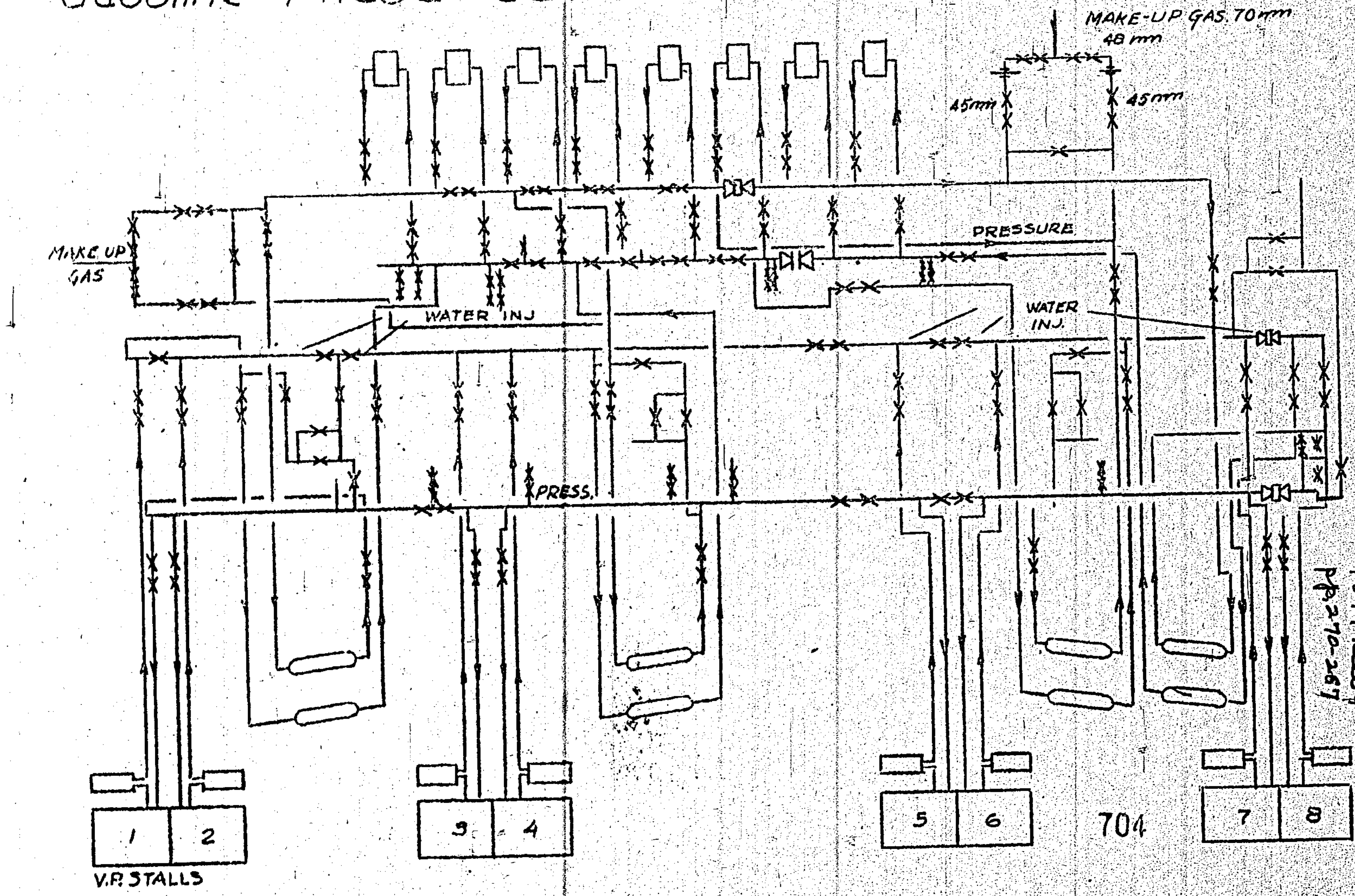
Vapor Phase

	1/15/1942 (no hydrate formation)				1/28/41 (format. of hydrates)	
Stall	6434 (stalls 3,4,5)		5058 (stalls 6, 7,8)		Stall 4 (6434)	
Circulation pump Pressure side, atm.	319		320		321	
Circulation pump suction side, atm.	283		285		290	
Pressure where hydrates formed	—		—		300	
Water for heat exch. II, li/hr	500		500		500	
Water Product Cooler li/hr	800		1,000		500	
Water in Circuit	100		200		400	
Catchpot Water-free m^3/hr	10 - 13 each		16 - 21 each		15	
Catchpot Temper.	15 - 20°		15 - 20°		33 (temper. 10°)	
Outlet gas m^3/h	100,000 (3.4.5)		130,000 (6.7.8)		41,000 (4)	
Circuit Temp. Pressure side	34°		39°		27°	
Circuit temp. Suction side	19°		21°		19°	
Make-up Gas m^3/h	13,000 (3.4.5)		29,000		abt. 4,000	
Oil Scrubber	No oil scrubber needed					
	Pressure side	Suction	Pressure	Suction	Pressure side	Suction
Composition of Circulation Gas	CO_2 0.0	0.0	0.9	0.9	CO_2 0.3	0.0
	H_2S 0.0	0.0	0.0	0.0	H_2S 0.0	0.0
	O_2 0.0	0.0	0.0	0.0	O_2 0.0	0.0
	H_2 93.1	91.0	91.0	90.5	H_2 94.6	94.2
	CO 0.4	0.6	0.1	0.2	CO 0.0	000
	N_2 3.9	5.0	4.8	4.0	N_2 2.4	3.0
	Hydrocarb. 2.6	2.9	3.0	4.0	Hydrocarb. 2.7	2.8
	C-number 1.66	2.21	1.74	1.52	C-Number 2.76	3.0
	NH_3 0.003 g/m^3	0.004 g/m^3	0.009 g/m^3	0.054 g/m^3	NH_3 0.003 g/m^3	0.007 g/m^3
Composition of Make-up Gas	CO_2 0.0				CO_2 0.0	
	H_2S 0.0				H_2S 0.0	
	NH_3 0.0				NH_3 0.0	
	O_2 0.0				O_2 0.0	
	CO 0.0				CO 0.0	
	H_2 97.0				H_2 97.2	
	Hydrocarb 0.6				Hydrocarb. 0.5	
	C-number 1.0				C-Number 1.0	
	N_2 2.4				N_2 2.3	

Gasoline Phase Gas Circulation Scheme 300 Atm.



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pp 270-287

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

706

KCBraun
4-10-47

CORONENE
(Laboratory Experiments)

By Boente, Ludwigshafen
13 June 1944

A knowledge of ring systems more condensed than coronene would be very desirable for the study of the field of hydrocarbons from coronene to coke. The preparation of these highly condensed ring systems by synthesis, e.g. with the aid of phthalic acid or succinic acid anhydride, is too complicated and time consuming at the present time.

However, we can do considerably better by condensing coronene with $AlCl_3$. In the condensation of aromatics with $AlCl_3$ undefined brown powders are generally obtained, which appear as green fluorescence in a solvent. Test tube experiments in the condensation of coronene have shown the following interesting phenomenon:

(See Diagram)

Coronene condensed with $AlCl_3$, in the proportion of 1:2, for 2 hours @ 200°C, first produces a reddish brown substance. This probably consists of a conglomerate of various products of condensation. If, after removing the unchanged coronene, this product is heated to 500 - 600°C, most of the product of reaction is coked, probably the unstable (labile) ring systems, while luminous red needles sublimate from the hot coke. This hydrocarbon is insoluble in the ordinary solvent. At this high temperature it melts during coking. The substance appears to be a uniform hydrocarbon of coronene-like structure.

Since a small amount of this hydrocarbon, enough for experimental purposes, can be made in a comparatively short time, it would be desirable not to ship larger quantities of coronene outside, until the product of reaction has been more clearly defined.

HYDROGENATION, DEHYDROGENATION AND SPLITTING OF CORONENE WITH WS_2
(Autoclave Experiment)

1). The best hydrogenation temperature of coronene with catalyst 5058 is 14 mV (287°C), but hydrogenation already starts at 12-13 mV.

a) At low pressure, abt. 250 atm., 200 g coronene in decalene (decahydronaphthalene) solution can be used with 300 cc = 800 g catalyst. About 97% coronene is perhydrogenated. With greater concentration of the coronene based on the catalyst, the catalyst activity is reduced and an ever larger percentage of coronene remains unaffected when using larger quantities of it.

b) At high pressure, about 600 - 800 atm. greater concentrations of coronene, about 300 g coronene to 300 cc catalyst, can be used, whereby abt. 99% of the coronene is perhydrogenated.

2). At temperatures above 14 mV (287°C) partial dehydrogenation of the coronene takes place:

a) At low pressure, abt. 300 atm. the dehydrogenation temperature is abt. 21 mV (408°C). Since coronene and perhydrogenated coronene in the proportion of 1:1 form a relatively stable complex compound, apparently only half of the perhydrogenated coronene is dehydrogenated at first. The molecular compound formed herewith is then further dehydrogenated in part at higher temperature.

b) At high pressure, no appreciable dehydrogenation of the coronene takes place up to temperatures of abt. 23.5 mV (450°C). On the contrary, the perhydrogenated coronene will rather split up, provided the catalyst is not damaged by coronene.

3). In the hydrogenation of coronene, the splitting activity of the catalyst is reduced by the deposition of coronene and its other products of condensation on the catalyst.

a) At high pressure, results of experiments with the treatment of coronene in decalene solution with H_2 showed the following splitting up of the decalene:

Using 1000 cc decalene to 300 cc = 800 g
5058 @ 600-700 atm and 22 mV (425°C)

Coronene g	Splitting of decalene %	Splitting temperature for decalene
0	100	19 mV = 375°C
30	79	21 mV = 410°C
150	35	23.5 mV = 450°C
200	21	
340	18	
600	5	

b) At low pressure, the splitting activity of the catalyst was already reduced @ abt. 100 g coronene to 300 cc 5058 to such an extent that @ 425°C only 10% of the decalene was split up.

4). If we use perhydrogenated coronene in our experiments to split up the coronene, the activity of the catalyst is probably not reduced as much, and, in heating to 23.5-25 mV (450-476°C) @ 300 atm., 80-90% of the coronene is split up, while 10-20% of the coronene is dehydrogenated. (In these experiments we worked with and without decalene as solvent. In the latter experiment the decalene was split up 95%).

If we therefore, want to hydrogenate and split coronene, it is best to work with a low coronene concentration, about 2-3%, based on the catalyst, and a high H_2 partial pressure, about 700 atm.

If we want to work in 2 stages, the coronene is hydrogenated (prehydrogenation converter) in the first stage and the perhydrogenated coronene is split in the second stage (splitting converter).

5). In the experiments described above, we determined the quantity of organic matter adhering to 1 cm^2 of catalyst, and which could not be removed by exhaustive extraction with benzol and heating to 550°C with air excluded.

This organic matter equalled 5 to 6% in the coronene hydrogenation and dehydrogenation experiments and about 1 to 3% in the experiments with perhydrogenated coronene. The determination of C and H in this organic matter on the catalyst showed 4.2 gH to 100 g C. This corresponds to the theoretical value of the C and H analysis of coronene.

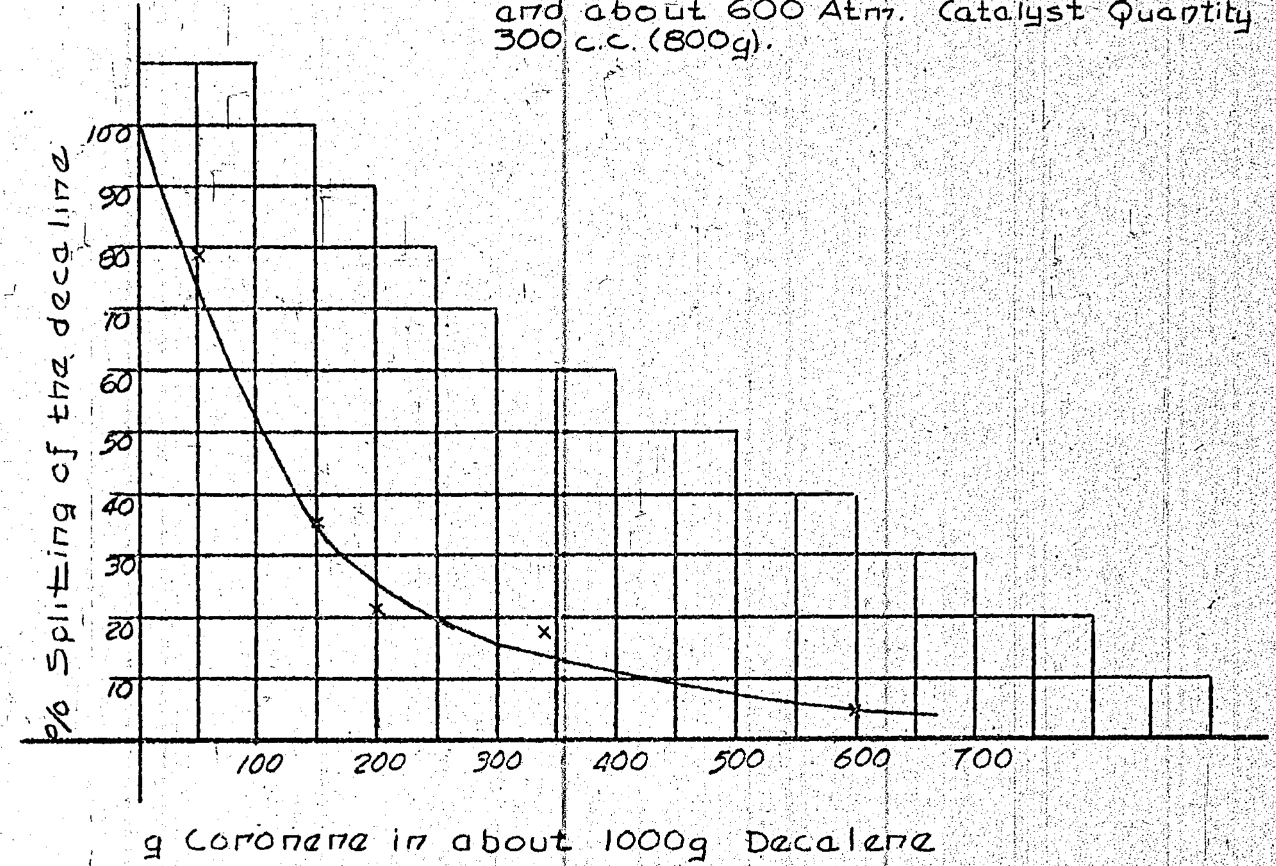
/pkl

Hydrogenation, Dehydrogenation and splitting of Coronene with WS_2

Quantity of Catalyst used = 300 cc (800g) 5058

Item No.	Auto-clave	Exper. No.	Date	Quantity				Press.			% Split Products of Decalene Boilg. Point to (Cumulative)			% Org. Subst. on the used catalyst	Remarks
					decalene	mV	°C	Start	Max.	End	150°C	170°C	180°C		
1	8	32	4-30-43	Without Coronene	1000	14 & 22	287 & 425	350	760	130	86.0	96.0	100.0	0.5	Decalene completely split
2	2	1264	4-30-43	150 g Coronene	850	14 & 22	287 & 425	150	395	120	--	0.2	3.4		Decalene slightly split, Coronene partly dehydrogenated
3	8	30	4-28-43	150 g Coronene	850	14 & 22	287 & 425	350	600	270	4.0	15.2	35.0	5.7	Decalene split 1/3 Coronene not split, slightly dehydrogenated
4	2	1265	5-4-43	150 g perhydr. Coronene	850	14 & 25	287 & 476	120	400	130	6.3	13.7	57.2	5.3	Decalene split 1/2 Perhydro-Coronene partly dehydrog.
5	8	33	5-4-43	150 g perhydro. Coronene	850	14 & 25	287 & 476	300	760	140	86.1	90.5	94.5	3.2	Decalene almost completely split. Coronene largely split, only little dehydrogenation

Splitting of Decaline with K-5058 in the presence of Coronene. @ 22 mv (425°C.) and about 600 Atm. Catalyst Quantity 300 c.c. (800g).



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U. S. BUREAU OF MINES 710 T-315
HYDRO. DEMON. PLANT DIV.

KCBraun
4-10-47

Nitrification of Chromium Steels in Catalytic Pressure Hydrogenation

By Dinkler & Reitz, Ludwigshafen, 12 July 1941

Summary

In a converter of N10 alloy steel which had been operating for some months in 700 atm liquid as well as vapor phase (aromatization), an increase in the nitrogen content of abt. 0.2% was found in a surface layer of abt. 0.5 mm depth. A surface impoverishment of vanadium could not be detected. This absorption of nitrogen represents only a fraction of the maximum possible under conditions of hydrogenation. In a preheater tube, in service for 3 years at Welheim, a much greater nitrogen content was found in the surface layer.

In connection with the question into the possibility of nitrification of chromium steels in catalytic pressure hydrogenation as a cause of trouble in operation, we examined a 40 liter converter of N10 steel, which had cracked near a weld (welded-on outlet nipple) at 510° C and 650 atm. The converter in question had been operated in Stall 703 for 2-3 months at 700 atm in the liquid phase and 1-1/2 months at 700 atm in aromatization when the trouble occurred. The crack was presumably due to excessive hardness of the material before fabrication and neglected heat treatment after welding.

After mechanically cleaning the surface, samples were taken from the inner wall by planing off 4 successive layers each 0.2 mm thick. These 4 samples were analyzed in Oppau by the Kjeldahl method, with the following results:

1. layer, 0.030%N, 0.82%V
2. " , 0.029 , 0.80
3. " , 0.011 , 0.77
4. " , 0.007 , 0.89

outer wall, 0.008%N, (abt. 0.8%V).

A nitrogen enrichment of over 0.2% in the surface layer penetrating to a depth of abt. 0.5 mm, is, therefore distinctly noticeable, while no deterioration in the vanadium content of the surface layer occurred. This absorption of nitrogen is still below the maximum possible. Compare Report 18622, by Dr. Reitz, of 10 May 1941, according to which a nitrogen content up to about 0.8% in a depth up to about 0.2 mm is possible. The overall operating time of this converter, see above, was much shorter than with industrial size converters, so that a still greater nitrogen absorption must be figured on.

According to Dr. Class of the materials testing laboratory at Ludwigshafen, an examination of the burst N10 preheater tube from Welheim showed 0.18% N_2 in the surface layer of the inner wall. This represents a much greater increase in N_2-content, corresponding to the much longer operating period of about 3 years. The same tube was examined at Krupp Works, where an N_2-content of 0.3% was found in the inner surface layer. The difference between these figures is probably due to a difference in the thickness of the layers from which the samples were taken.

/fkp

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High-Pressure Research Lu 558
December 4, 1941

Translated by:
H. J. Kandiner*

REPORT ON STATUS OF LITERATURE ON GAS HYDRATES

(Presented by Dr. Nonnenacher at the Research Progress Conference held at Ludwigshafen on December 4, 1941)

Considerable work has been performed in America in the last ten years to obtain a clear concept on the properties of gas hydrates. The purpose for this is obvious since gas hydrates occurring in underground natural gas pipe lines may plug the line and cause considerable expense in excavation and repair. Gas hydrates themselves have been known for a long time. Humphry Davy in 1810 discovered the first gas hydrate by cooling damp chlorine gas to 0°C. (ref. 1). In the years 1838 to 1890, Villard discovered that hydrocarbons such as methane, ethane, propane, acetylene, and ethylene formed gas hydrates. At the present time, a large number of gases are known which may form hydrates. Iso-butane and n-butane are the largest saturated hydrocarbon molecules for which the observance of hydrate formation has been made with certainty. In addition, CO_2, H_2S, and CH_3SH form hydrates. These compounds have the following properties: They are white crystalline combustible materials which have a greater volume than water, similar to ice. Under conditions in which they are not stable, the hydrates decompose into gases. This decomposition takes place with a crackling noise. The aqueous vapor pressure of the hydrates is smaller than that of water at the same temperature. So, for example, if damp propane which is saturated with water vapor at 3.3°C. (under which conditions the hydrates is the stable phase) becomes converter to a hydrate, the condensation point of the gases drops some 7°C.

A thorough-going experimental study of methane and ethane hydrates was performed by the American research workers, O.L. Roberts, E.R. Brownscombe, and L.S. Kore (references 4 and 6). W.J. Wilcox, G.D. Carson, and D.L. Katz, (ref. 7) investigated propane and n-butane hydrates.

(The next paragraph is a description of the experimental equipment used by Roberts and others.)

Figure 1 gives the melting point curves for the hydrates of methane, ethane, propane, and n-butane. Pressure is plotted logarithmically. From the melting point curve from ethane hydrate, it can be seen that at 0°C. a pressure of 2.8 atmospheres is needed for hydrate formation; at 10°C., 8 atmospheres,

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*Chemical Engineer, U. S. Bureau of Mines, Research & Development Division, Office of Synthetic Liquid Fuels, Pittsburgh 13, Pennsylvania and at 20°C. approximately 250 atmospheres. The critical temperature above which no hydrate formation occurs without regard to pressure is approximately 21.5°C. The melting point curves for ethane, propane, and n-butane are different from that of methane in the following regard: They show a characteristic temperature at which they suddenly increase very markedly in slope. The significance of this temperature is that beyond this temperature, it is practically impossible to form gas hydrates. For ethane hydrates, this critical temperature is 14.5°C., for propane hydrates, 5.6°C., and for n-butane hydrates, approximately 1.1°C. At temperatures greater than these values, hydrates of these gases can no longer be formed at practically all pressures. These critical temperature points represent quaternary points at which the hydrocarbon in the gas-phase, liquid-phase, the solid hydrate, and liquid water are all in simultaneous equilibrium. The melting point line below the critical temperature points represents the equilibrium between gas and liquid water on one side and gas and hydrates on the other. The melting point above the quaternary point is the equilibrium for liquid hydrocarbon and water on the one hand, and liquid hydrocarbon and hydrate on the other.

Figure 2 gives the total pressure-temperature diagram for the formation of methane hydrates from methane and water. Hydrate formation can take place at any pressure such that a portion of the methane-water vapor mixture is condensed. In the presence of liquid water, for example at 1°C. and 40 atmospheres, the formation of methane hydrates will take place in the solid form. If the drying of the methane gases is carried out to a sufficient extent that no water in the liquid phase can be present, and as can be seen from the equilibrium diagram, hydrates are no longer possible in the solid phase.

A more exact investigation of the diagrams for the hydrates shows that these compounds have the formula: Hydrocarbon·$7H_2O$. Approximately 5 kilograms of H_2O are found to every cubic meter of hydrocarbons. If more than 5 kilograms H_2O/m^3 hydrocarbon are employed, then liquid water will be obtained together with solid hydrates. Elimination of plugging of tubes carrying gases caused by hydrate formation can therefore be obtained by the utilization of large quantities of water injection. Up to the present date, only very few investigations of hydrocarbon gas mixtures and their hydrates have been made. Figure 3 gives data for two natural gases taken from the data of Wilcox, Carson, and Katz. From this figure, it can be seen that a gas containing 86.4 percent methane, 6.47 percent ethane, 3.5 percent propane, and 2.13 percent butane, formed hydrates at 25°C. This temperature is 3.5 percent higher than the critical temperature for methane hydrates. Apparently, hydrocarbon gas mixtures with a high percentage of methane have a higher quaternary point for hydrate formation than the corresponding critical point for pure methane. In any case, by extrapolation of the curves of Figure 3, it can be seen that at temperatures of above 35°C. practically no hydrates can exist quite without regard to pressure no matter how high.

From the foregoing material, it is apparent that the practical procedures for avoiding hydrate formation are threefold: (1) lowering of pressure, (2) heating of the gas lines, or (3) drying of the gases.

Dehydration of the gases can be most expediently performed by injection of a drying fluid into the gas line, for example, alcohol or a calcium chloride solution. According to Hammerschmidt (references 2 and 3), by injection of an 18 percent calcium chloride solution, the formation of hydrates in a natural gas pipe line at 40 atmospheres at 1.7-3.3°C. was avoided. In the United States, the most frequently used methods for drying the gases are cooling, compressing, or passage over drying agents, (or, of course, by combination of these other methods). Figure 4 gives physical data for drying process using calcium chloride solution. For example, if it is desired to drop the dew points of the gas from 7.1°C. to -3.9°C., it is necessary to use a 35 percent calcium chloride solution. The principal shortcomings of this practice is in the serious corrosion encountered. In order to avoid corrosion, it is necessary that noble metals be used in contact with the solution, and no oxygen permitted into the system. Also, it is advantageous to use weakly alkaline solutions. In addition to calcium chloride solution, technical purity 96 percent diethyleneglycol, 85 percent glycerine, or lithium chloride and zinc chloride solutions may be used. The following table gives a brief summary of dew point lowering at temperatures of 32°C. and 4.4°C. for these various materials.

Solution	Dew Point Lowering at 32°C.	Dew Point Lowering at 4.4°C.
LiCl	37	22
$ZnCl_2$	31	22
Diethyleneglycol (96 percent)	28	25
Glycerin (85 percent)	18	17
$CaCl_2$	17	13

In the United States, plants have recently been erected employing solid adsorbents, such as calcium chloride, silica gel, sodium hydroxide, and/or alumina. Using these agents practically completely dry gases can be readily obtained.

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4 O.L. Roberts, E.R. Brownscombe, and L.S. Howe, "Methane and Ethane Hydrates". Oil & Gas J., December 1940, p. 37.

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6 O.L. Roberts, et al., Pet. Eng. 12, No. 6, March 1941, p. 56.

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FIG. 1.
MELTING POINT CURVES FOR C_1-C_2-C_3-C_4 HYDRATES.

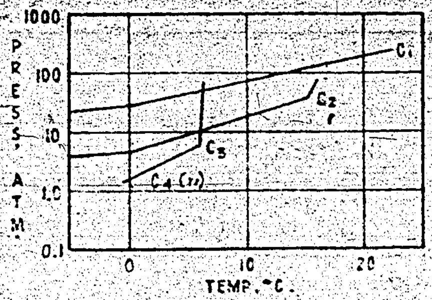
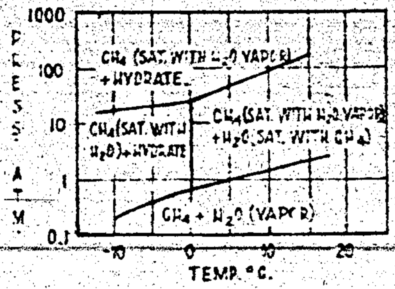
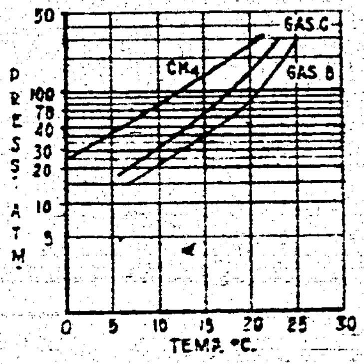


FIG. 2.
CH_4 HYDRATE - H_2O - CH_4 SYSTEM
(99% CH_4 : 1% H_2O)



	GAS B.	GAS C.
N_2	.0264	.0043
CO_2	----	.0051
CH_4	.8641	.9320
C_2H_6	.0647	.04[illegible]
C_3H_8	.0357	.0161
iC_4	.0099	----
nC_4	.0144	----
C_5 +	.0078	----

FIG. 3.
MELTING POINT VS. TEMP. CURVES FOR SEVERAL GASES



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Translated by:
H. J. Kandiner*

GAS HYDRATES

Summary

Several approximate calculations on the possibility of gas hydrates formation were made based on literature researches and some data from certain of the plants. Although, because of the absence of experimental data, a number of significant factors were not considered (such as the influence of CO_2 and H_2S on hydrate formation, the influence of the hydrogen partial pressure, etc.), the calculated curves agree quite well with the observed behavior of plant systems. The circulating gases are always saturated with water since water is sprayed into the circulating stream in all hydrogenation plants (with the exception of Mersersburg). Thus water in the liquid phase is probably always present, and gas hydrate formation can take place at appropriate pressure-temperature-composition conditions.

Calculations are made below for the liquid- and vaporphase hydrogenation plants showing the temperature-hydrocarbon partial pressure regions in which gas hydrate formation is possible. These results are then compared with the observed plant behavior 1/.

The attached figure is an approximate gas hydrate phase diagram. Below and to the right of the indicated curve, gas hydrate formation is improbable; whereas above and to the left of the curve, gas hydrate formation is possible. The calculations show that the possibility of gas hydrate formation is comparatively independent of the composition of the hydrocarbon gas mixture in the circulating gas. Hence, as a first approximation, the temperature of incipient gas hydrate formation can be directly related to the total partial pressure of the hydrocarbon gases in the circulating gas stream.

In a 600-atmosphere hydrogenation plant (liquid- or vapor-phase type), the partial pressure of hydrocarbon gases prior to the absorption units on the suction side of the circulating circuit amounts to approximately 200 atmospheres. This corresponds to a temperature for gas hydrate formation of 29°C. Even if some of the gas taken from the compressor outlet side of the recirculation circuit is blended back into the suction side, the partial pressure of hydrocarbons will drop only to 140 atmospheres. At this partial pressure, the limiting temperature for gas hydrate formation is only 1-2°C. lower or approximately 27-28°C. In order to avoid gas hydrate formation, it is therefore necessary for the temperature of the recirculating

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1/It was assumed that no more than 5 percent $CO_2 + H_2S$ was present in the circulating gas.

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gas stream on either the suction or pressure side of the circuit, to be in excess of 35-40°C. In the 300-atmosphere hydrogenation plants (liquid- and vapor-phase), a somewhat lower temperature can be used to prevent the formation of gas hydrates, depending of course on the partial pressure of the hydrocarbons in the circulating gas. If the partial pressure of the hydrocarbons in the recycle gases is approximately 100 atmospheres, a temperature of 30-35°C. is sufficient; at 50 atmospheres partial pressure of hydrocarbons, 25-30°C. suffices.

It must be borne in mind, that the calculations presented here are only tentative and are intended as a preliminary estimate. Experimental studies should be undertaken to determine the phase diagram for gas hydrate formation with greater certainty. Also, investigations on the influence of inert gases, introduction of oil, alcohol, and other liquids at high pressures, and certain experiments with pure gases and gas mixtures must be performed.

Several calculations were made for certain hydrogenation plants on the possibility for formation of gas hydrates in the liquid- and vapor-phase circuits. The results of these calculations are then compared with experimental observations on the plants, expecially where gas hydrates were observed.

The data from the plants report only total hydrocarbon content and not the subdivision into C_1,C_2,C_3,iC_4, and nC_4. Hence, it was necessary to approximate the distribution of hydrocarbons in order to perform the calculations.

In all plants, with the exception of Magdeburg, water is injected into the circulating gas stream. The quantities of water vary between 0.3 to 4.2 kilograms per 100 cubic meters of circulating gas, or, recalculating, from .01 to 3.0 kilograms per cubic meter of hydrocarbon gas. In the lines between the water injection and water removal steps, the presence of aqueous water is always probable, and hence, gas hydrate formation at the appropriate temperature-pressure relationship may occur. Incidentally, even these quantities of water do not always guarantee avoidance of plugging lines by gas hydrate formations 2/. Figure 1 was used to calculate the curves for gas hydrate formation on the temperature-pressure diagram in the presence of aqueous water. The phase diagrams of the hydrates of pure hydrocarbons (methane, ethane, propane, and n-butane) were taken from the literature and are shown as diagram 1 of Figure 1. These curves have already been discussed at the general conference on research of December 4, 1941. According to the researches of Deaton, Frost, and others, the gas hydrates of hydrocarbon mixtures behave similarly to solid solutions. Diagram 3 of Figure 1 presents some data from the work of Hillard, Wilcox, Carson, and Katz. This work was performed at a temperature of 35°F. or 1.7°C. The values of K are plotted logarithmically against pressure, where K is defined as the ratio of mole percent of the constituent in the gas phase divided by the mole percent of the same constituent in the gas hydrates 3/. If Raoult's law can be applied to the system,

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2/Hammerschmidt reports, from the American practice, that introduction of .5 kg. H_2O/m^3 of recycle gas did not prevent the formation of gas hydrates.

3/The experimental basis for the various curves is very questionable, particularly for n-butane: Iso-butane appears to form no solid solutions with other hydrocarbon hydrates (?).

then the curves of diagram 3, Figure 1, must be straight line with a slope of -1.

If at the given temperature (1.7°C. in diagram 3, Figure 1) P = the total pressure of the gas mixture, p = partial pressure of a given component in the gas mixture, z = mole fraction of the same component in the gas phase, x = mole fraction in solid phase, and n = decomposition pressure of the pure gas hydrate of this particular component, then by the Dalton-Raoult law we have

$$p = z\,P = x \cdot n, \text{ or } K = \frac{z}{x} = \frac{n}{P}, \text{ so that } \log.\ K = \log.\ P - \log.\ n.$$

Hence, if log K is plotted against log P, straight lines with a -1 slope should be obtained. As can be seen from diagram 3 of Figure 1, the values of log K fall considerably more rapidly than this slope would indicate. In the case of n-butane, at higher pressures, the curve actually reverses itself. This behavior appears to be characteristic of the less volatile constituents of a gas system. Diagram 2, Figure 1, gives curves (taken from the same source as diagram 3) for the formation of gas hydrates for three natural gases. By comparison of diagrams 1 and 2, it can be seen that in place of the sharp breaking point observed in diagram 1, a bend is found in diagram 2. This bend is flatter with smaller values of average hydrocarbon content. As a first approximation, the curves of Figure 2 may be regarded as two straight lines which intersect one another. In the same way that for the pure hydrocarbons the breaking point on the gas hydrate curve is related to the vapor-pressure curve, then, in diagram 2, the approximate location of the bend in the curve for hydrocarbon mixtures may be taken as the intersection of the dew-point line for the gas mixture with the gas hydrate curve. For conditions above the critical, the dew-point line is obtained by linear extrapolation. The dew-point curve for gas mixture B above the critical[4] is indicated as a dotted line in diagram 2 [5].

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[4] The critical point for curve B lies most probably in the vicinity of 10°C.

[5] Average values taken from the literature were used for the calculations. Some of the calculations were based on vapor-pressure data and some of them on the equilibrium vaporization contents for binary systems. The constants used are given in supplement 3. See also, Ind. Eng. Chem. the following references: 24, 517; 26, 352; 32, 118; 352, 817, 1085.

There is no data in the literature for the formation of gas hydrates of iso-butane or for the effect of CO_2 and H_2S on gas hydrate of methane, ethane, propane, and n-butane. In addition, very little data on the influence of hydrogen partial pressure is available. The calculations made all omitted the effect of these factors. From diagram 3, the pressure for the beginning of gas hydrate formation as well as the approximate composition of the hydrate at a temperature 1.7°C. was estimated. For gas mixtures having an average C of approximately 1.32, the remaining path of the curve was extrapolated based in part on diagram 2. For gas mixtures having higher average C, the gas hydrate curve to the point of intersection with the correspondingly calculated dew-point curve was approximated from diagrams 1 and 2, and then extrapolated with a somewhat steeper slope than would be obtained for the calculations performed by diagram 2. The uncertainty of these calculations is estimated at being ± 3°C., assuming of course that the data of Figure 1 are correct.

A sample calculation on the liquid-phase circulating-gas from the Welheim plant will clarify the procedure. The hydrocarbon gas mixture has the following composition: (compare with Figure 2 gas a): Mole percent CH_4-57.2; C_2H_6-22.9: C_3H_8-13.2; nC_4H_{10}-4.6; iC_4H_{10}-0.9, and C_5H_{12}-1.2.

Calculation of the Pressure for the Beginning of Gas Hydrate Formation and Composition of Gas Hydrate at a Temperature of 1.7°C.

From the given composition, the gas hydrate "formers" are estimated as: Mole percent CH_4-58.4, C_2H_6-23.4, C_3H_8-13.5, nC_4H_{10}-4.7.

At incipient gas hydrate formation, the mole fractions Zi of individual components in the gas phase have the values given above, and we shall let X_i be the corresponding mole fractions in the solid phase. From diagram 3, we estimate that at a pressure of 3.6 atmospheres, the summation of X_i equals 1; and hence, at this pressure, gas hydrate formation occurs. The gas hydrate has the following composition: CH_4-0.15, C_2H_6-0.75, C_3H_8-0.34, and nC_4H_{10}-0.57, where all the values are mole fractions.

Calculation of the Dew-Point Curve

An incipient condensation the mole fraction of the individual component from the gas phase is given by the composition above for CH_4, C_2H_6, C_3H_8, C_4H_{10}, and C_5H_{12}. Let X_i be the mole fractions in the liquid phase.

At a temperature of 0°C. We calculate that at a pressure of 7 atmospheres, the summation of X_i is equal to .82, and at a pressure of 14 atmospheres, the summation of the X_i = 1.35. By linear interpolation for $X_i = 1$, the pressure is 9.4 atmospheres. The values of $K_i = Z_i/X_i$ were taken from supplement 3.

At a temperature of 10°C. A similar calculation shows that summation X_i at 14 atmospheres is 1.02, and at a pressure of 21 atmospheres, the sum of X_i is 1.29. By linear extrapolation summation $X_i = 1$ at a pressure of 13.5 atmospheres. Hence, at 0°C., the dew point is 9.4 atmospheres and at 10°C., a dew point is 13.5 atmospheres.

As a first approximation, on a log P vs. T diagram, the actual dew-point line should lie pretty close to a line drawn through these points [6].

Approximate Extrapolation of the Remaining Course of the Gas Hydrate Curve

Since the gas mixture under study contains more propane and n-butane than the natural gas of diagram 2, Figure 1, and since the gas hydrate curves for n-butane and pure propane are somewhat steeper than those for pure methane and ethane, the gas hydrate curve should have a steeper slope up to the point of intersection of the dew-point line than the corresponding curve for the natural gases. By graphical estimation, the slope was approximated at 1.3. The second portion of the gas hydrate curve beyond the intersection of the dew-point line must also be somewhat steeper than the curve for natural gases. As Figures 2 and 3 show, the observations agree quite closely with the calculations. Only in one case (Wesseling liquid phase) was gas hydrate formation observed at a temperature which was several degrees above the calculated limit for gas hydrate formation. It is possible that this discrepancy

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[6] For hydrocarbon mixtures which have so small an average C content, that the critical period lies approximately in the range from 5 to 15°C., we can extimate the dew points at -12°C., and 0°C. Plotting the approximate dew point through these points and extrapolating through the critical region will give an approximate location for the dew point line in the temperature region desired.

can be attributed to our disregarding the effect of higher CO_2 and H_2S contents in this gas.

Undoubtedly, higher partial pressures of hydrogen increase the vapor pressure of the hydrocarbon and cause a distortion of the dew-point line towards lower temperatures and higher pressures. A similar effect is also probable on the curve for the beginning of gas hydrate formation. In any event, it is not possible at the present time to estimate the overall effect of hydrogen pressure.

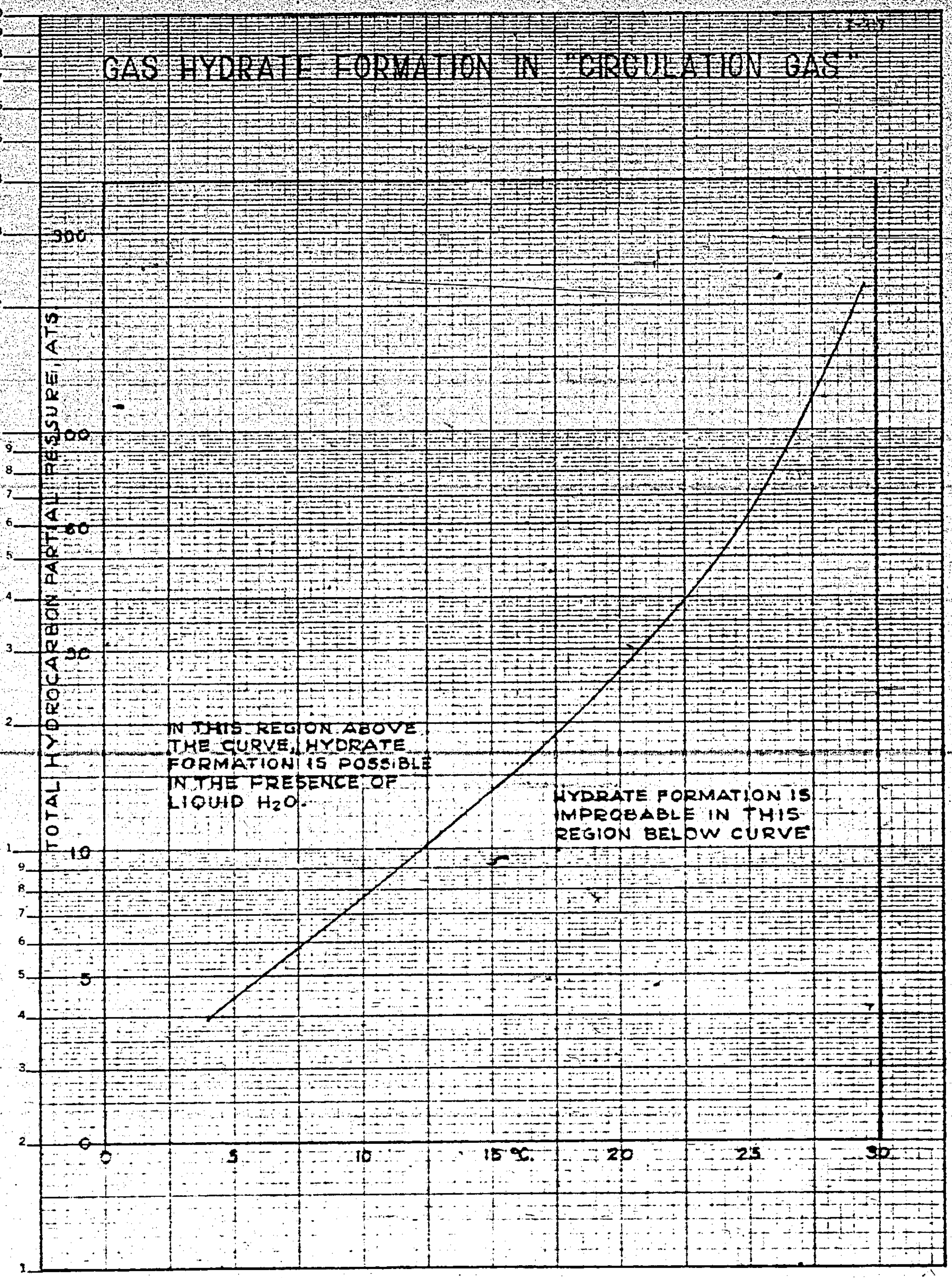
Supplement 3
(For calculation of the Dew-Point Curve)

Smoothed Values of Equilibrium Constant

$$k = \frac{\text{Mol Percent in vapor}}{\text{Mol Percent in liquid}}$$

of methane, ethane, propane, n-butane, iso-butane, and pentane for various values of T and P

Pressure, atmospheres	CH_4	C_2H_6	C_3H_8	nC_4H_{10}	iC_4H_{10}	C_5H_{12}
		Temperature, -12.2°C.				
14	7	1.3	0.34	0.086	0.12	0.030
21	5	1.0	0.26	0.07	0.10	0.024
		Temperature, 0°C.				
3.5	30	5.2	1.4	0.34	0.48	0.12
7	15	2.6	0.7	0.17	0.24	0.06
14	7.5	1.42	0.41	0.11	0.16	0.037
21	5.5	1.08	0.32	0.085	0.12	0.032
28	4.3	0.90	0.28	0.071	0.10	0.025
35	3.9	0.80	0.25	0.065	0.092	0.029
		Temperature, 10°C.				
3.5	36	6.0	1.8	0.48	0.68	0.180
7	17.5	3.0	0.90	0.24	0.34	0.090
14	8.5	1.7	0.51	0.16	0.226	0.055
21	6.2	1.24	0.41	0.126	0.178	0.045
28	5.1	1.05	0.37	0.105	0.148	0.039
35	4.5	0.90	0.32	0.095	0.134	0.035
42	3.75	0.75	0.30	0.090	0.126	0.053
49	3.2	0.64	0.23	0.085	0.120	0.035
56	2.8					
		Temperature, 15.6°C.				
3.5	42					
7	20	3.1	1.0	0.30	0.45	0.011
14	9.5	1.83	0.60	0.185	0.28	0.067
21	7.0	1.36	0.47	0.149	0.22	0.052
28	5.5	1.14	0.40	0.129	0.19	0.046
35	4.8	0.97	0.36	0.117	0.17	0.041
		Temperature, 21.1°C.				
3.5	50					
7	24.5	4.0	1.17	0.35	0.54	0.136
14	12.2	2.0	0.67	0.2	0.32	0.084
21	8.1	1.45	0.51	0.17	0.26	0.069
28	6.1	1.2	0.44	0.15	0.23	0.059
35	5.0	1.0	0.40	0.13	0.20	0.050
42	4.0		0.333	0.12		
49	3.4		0.375	0.116		
56	2.9		0.352	0.115		



GAS HYDRATE FORMATION IN "CIRCULATION GAS"

Carbonization

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

KCBraun
4-10-47

CHARACTERISTICS OF BITUMINOUS COAL LOW TEMPERATURE CARBONIZATION PROCESSES

By Dr. Braus, Berlin
25 Nov. 1941

In bituminous coal low temperature carbonization (schwelen) we can differentiate between three processes:

1). Flushing Gas Process (Lurgi-Spülgasverfahren)
2). Heating Surface Process (Koppers-Heizflächenverfahren)
3). Combination Process, based on Heating Surfaces (Didier).

No. 1). The flushing gas process, represented solely by Lurgi, brings all the heat required to the coal directly with the flushing gas. The greatest tar yields are obtained with it, which are 90% of the Fischer analysis. The proportion of oils of marine fuel oil quality in this process is 55 to 65%, based on the total pitch and tar yields, not including the gasoline yield. The properties of the fuel oils obtained by this process are not as good as those of the oils obtained by the other processes. However, the fuel oils obtained by the Lurgi flushing gas process meet all requirements specified by the navy.

The L.T.C. gas obtained in this process, which is, in part, available as excess L.T.C. gas, is diluted with nitrogen in its production and has a heating value of only about 2000 kcal/m^3. However, this gas may also be obtained free of nitrogen, if a concentrated gas is desired. For this purpose the gas is burned with oxygen instead of with air in the oven. (Auschwitz method).

One advantage of this process is the fact that it has been used for years in the carbonization of brown coal on the largest scale. Consequently, the process has been tested in all its details and practically eliminates all risk when used for bituminous coal.

The plant costs for this process are the lowest. For a complete plant they equal about:

0.17 t iron each t/ann tar products, or
250.00 RM " " " "

No. 2). The heating surface process brings the required heat from the outside over heated walls of ceramic material as in the coke oven, or over metallic walls.

Koppers, Didier and Lurgi use ceramic material, while Brennstoff Technik (B.T. Process) and Krupp-Lurgi use iron oven-walls.

Because of the temperature gradient necessarily in the L.T.C. feed in this case, a certain cracking of the bitumen liberated from the coal takes place. The yield in tar products is correspondingly lower. It is around 75 to 80%, depending upon whether overheating is prevented by suitable means, such as decreasing the chamber widths. The quality of the tar oils recovered in this process is decidedly much better than in the flushing gas process. Since at present, as explained in (1) above (?) no higher valuation of the fuel oil from these processes or a lower credit for the fuel oils from the flushing gas process is being considered, the heating surface process figures inferior to the flushing gas process, because of its low overall yield in tar products.

One advantage claimed for the heating surface process is that the quality of coke is said to be superior. However, we could obtain no verification of this claim. These processes are still in the first stages of development. Their use at this time implies a corresponding risk.

The processes using iron chambers are limited to temperatures of about 650°, or, at most, 700°C. At higher temperature the metal would wear rapidly. It is, therefor, difficult or impossible to produce a largely degasified coke, as used for certain purposes, such as carbide furnaces or buna works.

The excess gases in the heating surface processes are naturally concentrated @ abt. 4000-5000 kcal/m3.

Construction costs of all heating surface process plants we inspected were on the average 20% higher than for the flushing gas process. The Koppers bid for the Auschwitz plant was especially high, from which the following figures are derived:

0.300 t iron each t/ann tar products
450.00 RM " " " "

No. 3). The combined processes, recently represented and pushed by Didier and Kollergas, are heating surface processes, which operate the oven with a certain amount of flushing gas. The thruput can thereby be almost doubled. Because the L.T.C. gases are taken away faster from the coal, they are less cracked and the tar oil yield is higher than in the simple heating surface processes. In his bid for Auschwitz, Didier guaranteed a tar yield of 85.5% tar. This process will certainly be well under control in the near future and widely used and the properties of the tar products varied.

In the heating surface processes, as well as in the combined processes, much greater wear and tear of the plant and cost of repairs than in the flushing gas process must be figured in the cost of product.

Specific investment figures are:

0.200 t iron each t/ann tar products, or
328.00 RM " " " "

General

Generally speaking, business in the field of bituminous coal low temperature carbonization is in full swing in every respect. The processes can be economical only when the recovered tar products do not bring too low a price and the coke is of such quality that it may be utilized further. If the district of Upper Silesia is used as a basis for consideration, a powerful momentum for the carbonization of bituminous coal must be recognized in the fact that only a very limited number of coals there are suitable for producing the normal blast furnace coke. With the extraordinarily big expansion of industry in Upper Silesia, already underway or expected, a demand for coke must develop, which cannot be satisfied with existing facilities. The coke required can be supplied only in the form of L.T.C. coke. This momentum, therefore, will furnish the greatest incentive for the building of L.T.C. plants in Upper Silesia.

As already mentioned, the economy of carbonization, besides the evaluation of the coke, is decisively influenced by the value and market for the residual tar products, gasoline, oil and pitch. A closer estimate of the value of the various competing carbonization processes will be possible only when more and more accurate figures, particularly from large scale operations are available on the capacities of the processes and the nature of the different products produced by them.

/pkl

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

T-319

KCBraun
4-11-47

Pressure Drop in Liquid Phase Circuit and Vapor Phase Converter

A. - Pressure Drop in Liquid Phase Circuit.

By Hamacher, Ludwigshafen, 10 April 1942

The following specific resistance is obtained from thruput measurements before assembly:

Final Preheater, Pass I, W/Q^2	= 1.3 mm W.G./$(m^3/h)^2$
" " " III,	6.3
Drop Pipe in Pass III & Converter I	0.2
Electrical Preheater	1.4
Heat Exch., outside	0.2
" " , inside, air cooler	11.5
Tier Cooler, Hot Catchpot	
" " , Cold "	
" " , Water Separator	
Total	20.9 mm W.G./$(m^3/h)^2$

For Operating Condition when Starting-Up:

Circulating gas, incl. cold gas, $Q_1 = 2000\ m^3/h$, $S_n = 0.18\ kg/m^3$.
Pressure P = 300 atm.
Mean temp: 15 mV, equals 300°C, equals 573° absolute.
Pressure drop for resistance to flow:

$$\Delta p = 20.9 \times 2000^2 \times \frac{0.18}{1.15} \times \frac{1}{300} \times \frac{573}{288} = 0.868 \times 10^5 \text{ mm W.G.}$$

$$= 86800 \text{ mm W.G.} = 8.7 \text{ atm}$$

To this must be added the hydrostatic pressure

in Preheater, Pass I, 3 rising pipes @ 8900 mm kg	= 1.6 atm
" " " III, 5 " " @ 8900 "	= 2.7 "
" Elect. Preheater, 5 " " @10400 "	= 3.1 "
" the 4 converters	= 4.0 "
" Heat Exchanger, inlet pass (Hinweg)	= 1.0 "
" Tier Washer	= 0.5 "
Total Pressure Drop	= 21.6 atm

Resistances in Gasoline Converter 1001
After its Shut-Down, 9 January 1941

By Dr. Klinghardt, Gelsenkirchen-Horst, 3 February 1941

The attached diagram shows the resistances in Converter 1001, supplementing Dr. Klinghardt's report of 27 January 1941, for the purpose of equalizing as much as possible the errors of testing by layers. The diagram shows the normal resistance of a new converter of 105 mm W.G., corresponding to a resistance of 15 mm W.G. per layer of catalyst. The values found in layerwise testing on the dismantled converter average abt. 30 mm W.G. each catalyst layer, although a somewhat greater resistance was found in Layer I, due to crust deposits, while the greatest resistance of 108 mm W.G. is in the lowest Layer VII.

/fkp

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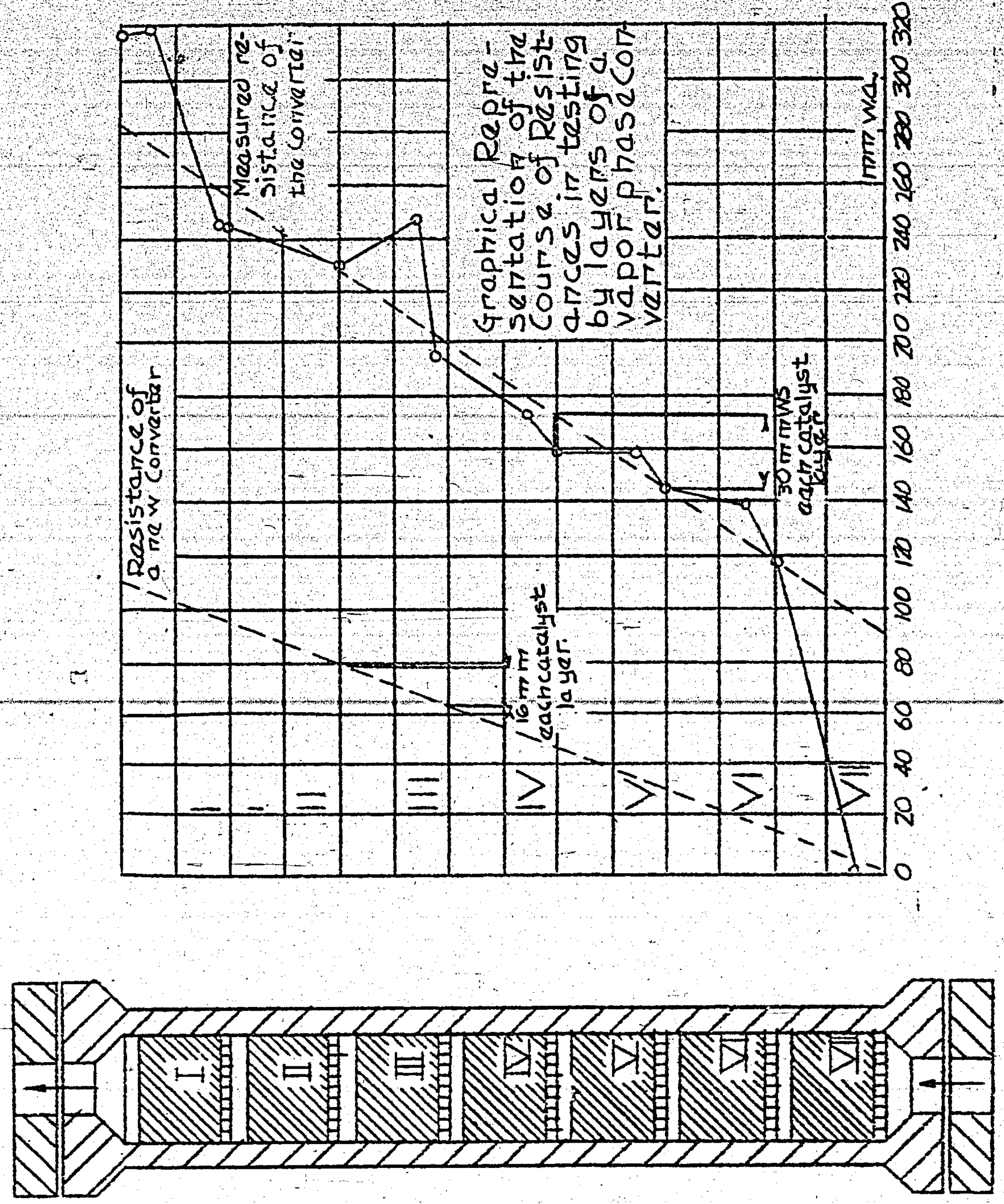

Graphical Representation of the Course of Resistances in testing by layers of a vapor phase Converter.
Resistance of a new Converter
Measured resistance of the Converter
16 mm each catalyst layer.
30 mm WS each catalyst layer
mm WG.
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320
I
II
III
IV
V
VI
VII

KCBraun/kp
4-11-47

HYGAS YIELDS IN LIQUID PHASE HYDROGENATION

By Hoelscher, Ludwigshafen, 3 June 1944

The following table shows results of hygas yields in liquid phase hydrogenation of Silesian coal in small and large scale experiments, compiled in Ludwigshafen, together with the latest figures from Pölitz and some older figures from Gelsenberg and Scholven for comparison.

The figures for ethane plus ethylene correspond to the yield at Blechhammer after extension I. (After completion of extensions II and III, this figure will be doubled.)

The ethane yield in % C of the C in the pure coal is the same for all coals and operating methods, within the limits of errors, apart from the radically deviating Pölitz values, which should probably be checked. Based on the ton of pure coal, the ethane yield, when running to gasoline plus middle oil, is naturally better, because of greater gasification.

T-320

730

TABLE I

Table I con't.

Li Ph-81

T-320
KCB

Coal	Mean of 6 Balances Heinitz	Mean of 12 Balances Heinitz	Beuthen-Heinitz 1:1	Mean of 3 Balances Beuthen-Heinitz 1:1	Beuthen-Heinitz 1:1	Heinitz	Pölitz Silesian Dry Coal			Gelsenberg (Dr. Becker 9-22-40) Zweckel			Scholven Podbi 8-25-37 Zweckel
% C	81.5	81.5	82	82	82	81.5	81.9			83			83
Operating Method	Gasol. + M-oil 600 atm	Fuel Oil 45% Aver.	Gasol. + M-oil	Fuel Oil 50% H'y Oil Exc.	Fuel Oil 35% H'y Oil Exc.	Fuel Oil 50% H'y. Oil Exc.	Gasoline + Mi-Oil 700 atm			To Auto-Gasol.	Date 3-8-40	To Auto-Gasol. + Fuel Oil	Gasol. + M-Oil 300 atm
Converter Size	10 ltr	10 ltr	Large Lu	Large Lu	Large Lu	Large Lu	Coal Liquid Phase Jan.	Febr. 1944	March 44				
Conversion (Pure Coal)	95.2	94.7	97.0	96.3	96.6		91.9	92.3	92.8				
Practical Oil Yield, t/m³/h.	0.50	0.714 (Thruput)	0.4	0.4	0.4								
Temperature °C	470.5	471	480	481	480								
Pract. Oil Yield, %/Pure Coal	56.7	61.5					52.5	52.5	54.0				
% C-Gasification/C in Pure Coal	based on gasif. 22.6 ±1.0 m.E.	18.2 ± 1.3m.E.	18.1	15.3	16.6		23.1	22.2	21.2	18.1	21.0	16.0 of conv. C	
H-C Gasification of Gasif. %	21 ±1.2 "	16.8 ± 1.4 "	17.2	14.5	15.8		21.8	20.6	19.8	17.2		15.2	
% C as CH_4	26.1 ±1.6 "	27 ± 0.9 "	26.0	31.5	29.7	30.6	15.7	17	18	24.4	24.5	24.4	21.5
C_2H_6	22.2 ±1.2 "	21.4 ± 21.4"	24.3	23.2	24.0	23.3	50.0	47.6	47.4	24.0	29.4	24.1	27.9
C_3H_8	32.8 ±0.9 "	32.1 ± 1.1 "	31.1	28.2	27.1	30.1	19.2	20.6	13.8	32.8	30.5	32.8	27.8
C_4H_{10}	18.9 ±0.2 "	20.0 ± 1.1 "	18.6	17.1	19.2	16.0	15.3	14.9	14.9	18.8	15.2	18.7	22.8
kg CH_4/t Pure Coal	59.5	49.3	52.1	51.3 ± 1.8m.E.	52.0	48.8	37.2			56		49.5	
C_2H_6	47.5	36.8	45.7	35.3 ± 1.8 "	39.7	34.6	110.0			51.5		43.7	
C_3H_8	68.5	52.6	57.1	42.1 ± 2.9 "	43.9	43.9	40			69		61	
C_4H_{10}	39.2	33.3	33.8	26.1 ± 1.8 "	30.7	23.1	32.5			39		34.3	
kg C_2H_4 + C_2H_6/t pract. oil yield	83.9	59.8											
t/ann C_2H_4 + C_2H_6/767000 Coal (OHW)	36400	27400	35000	27100	30400	26500	84400			39600		35000	
t/ann C_2H_4 + C_2H_6/767000 Coal + 45000 hot tar + 4000 weak gas producer tar	59700	29200	37300	28800	32400	28200	39600			42000		37300	

m.E. = Mean Error

T-321
KCBraun
4-14-47

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

H.O.L.D. Product Lines & Vessels in Louisiana
Comments on Drawing R-1016
By Dr. Frese, April 14, 1947

All products containing solids have a tendency to settle out the solids when at rest, thus causing clogging of the lines and consequent operating disturbances. Therefore, the construction of the vessels and location of the pipe lines must be suited to this condition. The following points should receive particular consideration:

1. The contents of the vessels should be kept in constant motion. This can be done either by stirring or recirculating the contents by a pump. To be safe, both methods were generally used in Germany on the most important operating parts. It may happen, e.g., that an agitator may fail, due to some cause or other, without the operator becoming immediately aware of it. The pump is intended for such a case and it prevents settling and plugging in the lower part of the vessel. Agitators are very often inadequate also because they agitate the bottom of the vessel very poorly, particularly with low liquid level, and the outlet pipe between the bottom of the vessel and the shutoff valve not at all. In this case also, the pump will provide the necessary operating safety.

2. Because of the danger of plugging up, the piece of pipe between the bottom outlet of the vessel and the first shutoff valve should be kept as short as possible. This is particularly necessary when no recirculating pump is provided.

3. The same thing applies to the connecting line between the vessel and the suction pump.

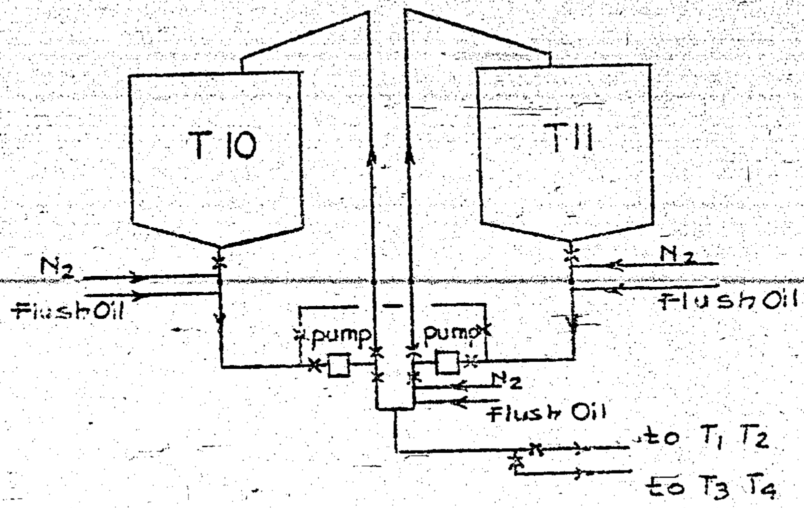
4. The connection for flushing oil and N_2 for blowing out the line is best made immediately behind the first shutoff valve at the vessel, not near the pump. Flushing or blowing out the line backwards, particularly against a full vessel, has very often been found to be inexpedient.

5. A product containing solids should be conveyed continuously from one part of the plant to another, even though in small quantities, rather than discontinuously. Blowing or flushing out a line is not always 100% safe and may occasionally cause clogging by forming plugs, which may stick in a pipe bend or ahead of a pump. Successful operation is dependent upon the reliability of the operator as well. Apart from special cases, blowing and flushing out of lines

should be done only before repairs, extended idleness, or after disturbances.

6. All dead pieces, i.e., parts of a line in which there is no flow, should be avoided with products containing solids. The valves and corresponding flushing oil connections should be arranged accordingly.

Based on these considerations, the following arrangement of lines at H.O.L.D. vessels T-10 and T-11 might be better than that shown on the drawing.



Continuous recirculation and agitation for both vessels is provided in this case. One vessel is being filled while the other is emptied. The quantity to be recirculated can ordinarily be kept small. A small measured quantity can be continuously pumped to T-1 and T-3. Two flow meters should be provided in this case, compared to one on the drawing, which measures the entire quantity, since the proposed pumping is not continuous. The pumps should be arranged so that they are interchangeable in case of repairs. Such a piping arrangement should prevent practically all disturbances.

In case it should not be possible to provide for recirculation, the shutoff valve at the vessel should in all cases be directly below the vessel. A poking device into the vessel from below should properly also be provided. This part has the greatest tendency to plug up. If the agitator should stop, the vessel should be emptied. Large deposits in the vessel are very troublesome in operation and at times require difficult hand-cleaning operations. The same thing may be said of the centrifuges, the storage tanks T-1 and T-2, the centrifuge filtrate tanks T-30 and T-31, and the pasting oil tanks T-3 and T-4.

The automatic level gage on the H.O.L.D. vessels V-26 and V-14 should properly be operated with bubble gas. The float system with flushing oil supply, shown on Drawing D-1107, is probably more costly and will cause more trouble.

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

KCBraun
4-15-47

Influence of Size and Density of 5058 Catalyst Tablets on Benzination and Prehydrogenation

By Reitz, Donath and others
Ludwigshafen, 7 Oct. 1943
(See also T-264)

Summary:

From the same charge of tungsten-sulfide, 10 and 3 mm tablets were made and 2 to 4 mm grains were screened from crushed 10 mm tablets. The 3 catalysts were compared with each other in the benzination of middle oil from Bruchsal oil and in the prehydrogenation of Scholven bituminous coal liquefaction middle oil with equal thruput, based on the weight of the catalyst, with the following results:

Benzination

Form of Catalyst	10 mm tablets	3 mm tablets	2-4 mm Grains
Bulk weight, kg/lit.	2.29	2.78	2.02
Gasif./Gasol. + Gasif.	→	3% decreasing	→
Gasol: Concentration	→	slightly increasing	→
Pentane Content &% - 100°C	← higher →	←	equal →
Aniline Point	←	equal	→
B - Middle Oil		somewhat greater hydrogenation & lower final boiling point	

Prehydrogenation

Form of Catalyst	10 mm tablets	3 mm tablets	2-4 mm Grains
Bulk weight (kg/lit)	2.29	2.78	2.02
Gasification	equal, based on injection		
Gasol: Concentration	← equal	→	lower
% - 100°C, A.P.	→	decreasing	→
Middle Oil: A.P.	→	rising	→

The smaller tablets and the grains, therefor, have distinct advantages over the larger tablets, from the chemical point of view, such as lower gasification and a B-middle oil more easily split, in benzination. In prehydrogenation they have the advantage of an H_2-poorer, i.e. a better anti-knock and more readily dehydrogenated, gasoline, and at the same time an H_2-richer, therefor more readily benzinated, middle oil.

In explanation it must be assumed that in the larger tablets the larger oil molecules are diffused with difficulty into the innermost zones of the catalyst, causing a decreased charge of the catalyst with larger molecules and, due to the centers of activity still available because of this, an increased charge of smaller molecules. This means a shift in the residence times on the catalyst in favor of the small molecules and to the disadvantage of the large molecules, from which the described observations may be derived.

The experiments are being continued with alumina catalysts, of importance to pre- and de-hydrogenation, and with benzination catalysts. If these experiments should indicate the same advantages of the small pill size as with 5058 and DHD, our large scale plants should be converted to the use of 6 mm pills as quickly as possible because of the advantages in thruput and gasification.

<u>Review of Experiments</u>

The experiments were made in 1 liter converter 315 with 10 mm and 3 mm pills and 2 to 4 grains from the 10 mm pills, made from the same batch of tungsten-sulfide and characterized by the figures in the following table:

(See next page)

Form of Catalyst	3 mm tablets	10 mm tablets	2 to 4 mm Grains from 10 mm tablets
Dimensions:	(Mean of 10 tablets)		(The grains had a laminous structure i.e. the thickness was considerably less than the other dimensions.)
Height h	3.921 mm	9.811 mm	
diam. $2r$	3.129 "	10.183 "	
volume r^2h	0.0302 cm^3	0.798 cm^3	
weight p	(Mean of 100 tablets) 0,139 g	3,022 g	
Apparent spec. grav. $d' = p/r^2h$	4.60 g/cm^3	3.79 g/cm^3	3.79 g/cm^3
True spec.grav. of WS_2 from literature, d	7.5	7.5	7.5
Bulk weight in 1 liter converter	2.780	2.290	2.015
Filling the catalyst space:			
Tablets or grains s/d'	60.5%/Vol	60.5%/vol	53.2%/vol.
of which WS_2, s/d	37.1 "	30.6 "	26.9 "
and pores $\frac{1}{d'} - \frac{1}{d}$	23.4 "	29.9 "	25.3 "
Voids betw. tablets or grains, $1-s/d'$	39.5 "	39.5 "	46.8 "
WS_2) in tablets pores) or grains	61.3%/vol 38.7 "	50.5%/vol 49.5 "	50.5%/vol 49.5 "
Load on Catalyst:			
Thruput, kg/l/h	0.97	0.80	0.70
" kg/kg.catal/h	0.349	0.350	0.348
m^3 gas/l/h	3.0	2.5	2.2
m^3 gas/kg oil	3.09	3.14	3.13
Relative resid. time in converter, calcul. fr. voids+ pores = catalyst space - WS_2	100	130	160

The catalysts were compared once under conditions of benzination with petroleum middle oil in a straight run and once under conditions of prehydrogenation with bituminous coal liquefaction middle oil, each at 2 temperatures. Because of the varying bulk weights of the catalysts, the thruputs were so chosen that they were alike, see above table. The properties of the injection feeds are shown in Table 1. Conditions and results of experiments are given in Table 2. The data on product analysis, yields, gasification, etc. are, in general, averages of 2 determinations. Table 3 shows the division of the products obtained in prehydrogenation into narrower fractions for determining the aniline point.

The following remarks may be made about the course of the experiments:

1. <u>Charge:</u>

1 liter 10 mm tablets K 5058/J, #1060 = 2275 g.
benzination, 12-15, April 1943.
prehydrogenation, 16-20, April 1943

2. <u>Charge:</u>

1 liter 10 mm tablets, as before, = 2290 g
benzination, 22 to 24 April 1943.

This experiment was discontinued after the converter was rapidly decompressed by a leak in a connecting line and we were afraid that the catalyst activity might possibly deteriorate because of this.

3. <u>Charge:</u>

1 liter 10 mm tablets, as before = 2290 g
benzination, 26-30 April 1943
prehydrogenation, 1-4 May 1943

4. <u>Charge:</u>

1 liter 3 mm tablets K5058/J, #1061 = 2780 g
benzination, 6-10 May 1943
prehydrogenation, 11-14 May 1943

5. <u>Charge:</u>

1 liter 2-4 mm grains fr. 10 mm tablets
K 5058/J, #1060 = 2015 g
benzination, 16-21 May 1943
prehydrogenation, 22-26 May 1943.

During the benzination experiment the converter leaked and was decompressed in the 19.5 mV period after the 18 mV period had been run without trouble. The experiment was continued after the trouble was corrected, since the catalyst had apparently lost none of its activity. (Yield before the interruption: Spec. Grav. 0.733, 14%-100°C, 45%-150°C, after the interruption: Spec. Grav. 0.736, 14%-100°C, 49%-150°C.)

Benzination was run without added sulfur, prehydrogenation with 0.5% CS_2.

Results of Experiments:

1. Benzination.

Benzination clearly showed differences between the various forms of catalyst under the conditions chosen, equal thruput with equal weight of catalyst. At 18 mV the gasoline concentration is practically the same for the three catalysts, while at 19 mV it increases somewhat in the order of 10-3 mm pills to the grains. No definite conclusion is, therefor, possible from these experimental data. The gasoline yield in the usual sense, i.e. based on catalyst space/h, runs generally parallel to the thruput. But if we base the yield on weight of catalyst, e.g. on 1 kg catalyst/h, as shown by the figures in parentheses in Table 2, its behavior is naturally the same as the gasoline concentration.

Although some doubts are attached to the figures for gasification, they still show the following:

Gasification is highest with the 10 mm pills and lowest with the grains, the difference being about 3% at both experimental temperatures. If we include the butane values, the decrease in gasification is principally due to a decrease in C_1-C_3 constituents while retaining the C_4 quantity, although the C_4 values for the 3 mm pills deviate somewhat. The values for isobutane content fluctuate so much that they were not included in Table 2.

Differences can also be recognized in the boiling curves of the gasolines. A greater percentage to 100°C is clearly obtained with 10 mm pills, and along with it apparently also a somewhat higher pentane content, than with 3 mm pills or grains. The 2 latter give approximately equal constituents to 100°C, while the C_5 values obtained with both experimental temperatures take different courses, though they probably don't vary much from each other. The increase in light constituents in the gasoline with 10 mm pills runs parallel to the increase in gasification, although an increase in the absolute quantity of butane and at least a constant relative quantity of butane could be expected, in contradiction to what has been said above about the quantity of butane. The butane contents obtained are, therefor, still in doubt, for the time being.

No differences are recognizable in the H_2-content of the gasolines. Nothing can be said about anti-knock quality, because most of the anti-knock values were lost in the explosion on July 29th.

Somewhat greater hydrogenation with 3 mm pills and grains than with 10 mm pills is obtained in the middle oils. Although the difference is small, it is worth noting, inasmuch as it shows up much greater in prehydrogenation, see below. At the same time the boiling point with 3 mm pills, and even more so with grains, is considerably lower than with 10 mm pills.

2. Prehydrogenation.

Still greater and more interesting differences than in benzination are obtained with the various forms of catalyst in prehydrogenation. Results obtained at the two different experimental temperatures also agree with each other here. Gasification, based on injection, seems to be practically the same in all cases. The yield in prehydrogenation gasoline is distinctly lower with grains than with 3 mm and 10 mm pills. H_2-content and %-100°C in the prehydrogenation gasoline distinctly decrease in the order of 10 mm-3mm pills - grains. The yield in light constituents shows, therefor, a behavior similar to that in benzination. On the contrary, prehydrogenation middle oil is poorest in H_2 with 10 mm pills. The experiment with 2-4 mm grains at the lower experimental temperature was apparently run at a too low effective temperature, compared to the experiment with pills. All in all, therefor, hydrogenation is shifted from the lower to the upper fractions in the conversion to smaller size catalyst. This is shown clearly in Table 3 and in curves of the aniline points, which are distinctly steeper for 3 mm pills and grains and cut the 10 mm pill curves at an average temperature.

Discussion of Results.

With equal catalyst load, i.e. equal thruput based on equal catalyst weight, as in these experiments, the smaller sizes of catalyst have distinct advantages over 10 mm pills.

In benzination we have the important advantages of lower gasification and more favorable B-middle oil characteristics, which are opposed only by the disadvantages of a somewhat lower pentane and %-100°C content of the gasoline. When the B-middle oil is recycled, which was not done here, the somewhat greater gasoline concentration with the smaller catalyst sizes should presumably show up still more distinctly, because the B-middle oil has a low final boiling point and is hydrogenated somewhat stronger, even though it isn't much. If we neglect the grain with its low bulk weight, since it cannot be considered for industrial application anyway, the 3 mm pills have a further advantage over the 10 mm pills. The results at hand were obtained in spite of a 20% greater density of the 3 mm pills. Consequently, with equal catalyst load, filling the catalyst space with more active material permitted a greater thruput and a greater yield with it. But a less dense catalyst could also be used, which would still give the tablets sufficient strength, by means of which the above named advantages of low gasification and better B-middle oil could possibly be enhanced.

In prehydrogenation the smaller catalyst shapes offer the advantage of weaker hydrogenation of the gasoline, which increases its anti-knock quality and makes it better suitable for DHD feed, as well as stronger hydrogenation of the middle oil and consequent easier benzination. We could also operate with equal aniline point of the middle oil or of the upper fraction of the middle oil, and thus obtain a gasoline still poorer in H_2 at lower temperature or increased thruput.

To explain the results one can imagine that the coarser oil molecules already have difficulty to diffuse into the innermost zones of the catalyst in the larger pills, as compared with the smaller pills or the grains. The result is a greater charge of the catalyst with the smaller, faster diffusing, molecules, which still get inside unhindered, and a lesser charge with larger molecules. This condition might also be expressed as a longer mean residence time of the smaller molecules and a shorter for the larger. The results can then be deduced from these assumptions almost by necessity.

As may be observed in prehydrogenation with large pills, the changed residence times must cause weaker hydrogenation of large molecules and at the same time stronger hydrogenation of the smaller molecule. The greater quantity of gasoline might perhaps be explained by an equally prolonged residence time of the oil constituents only slightly above the boiling range of the gasoline, e.g. those within the first third of the boiling curve of the oil.

In benzination, a correspondingly stronger hydrogenation of the middle oil and stronger splitting of the higher boiling constituents is to be expected with the smaller pills or grains, due to the increased residence time. This implies a lower boiling point on the one hand and increased gasoline concentration on the other. Conversely, with large pills the increased residence time of the gasoline constituents causes increased splitting of the heavy gasoline constituents to light gasoline and of the latter to gas.

The clearer advantages of the grains over the 3 mm pills is probably due to the fact that, in the grains, the distance between the inner zones and the surface is still smaller than in the 3 mm pills, because of their laminous structure, and also because the 3 mm pills were denser than the 10 mm pills and, therefor, also denser than the grains from the 10 mm pills. But the greater density must make the inner zones less accessible and, furthermore, produce fewer points of activity in the same weight of catalyst. Both effects, of course, are unfavorable.

Comparison With Previous Experiments

Experiments conducted by Dr. Krönig in 1931 compared 10 mm with 4 mm pills. In that case, however, the effect of the 32% greater density of the 4 mm pills was primarily apparent, while here the difference in density was only about 20% and at the same time, the difference in the size of pills, 10-3 mm, was greater. Contrary to the present experiments, the denser 4 mm pills then produced a greater %-100°C in the gasoline than the 10 mm pills. Moreover, only the gasoline yield was compared at that time, which was **lower with the denser catalyst,** based on the lower weight of the catalyst, but greater, based on equal volume of catalyst. Other experiments in 1931 by Dr. Simon with catalysts of various densities brought the same result as the above mentioned experiments.

In concurrent experiments by Dr. Peters in May 1943 (T-264) increasing gasoline concentration and slightly rising aniline points of the middle oil was also obtained with decreasing pill size in the benzination of Bruschsol gas oil. More precise data, particularly on the density of the pills used, which would permit a closer comparison with the experiments under consideration, are not contained in Dr. Peter's report.

Conclusions

Judging from results reported herein, a check of the influence of pill size on catalyst activity and quality of product would seem desirable with other types of catalysts, since a general application to them of these results is impossible without further consideration. Such experiments with alumina catalysts are under way. In case a similar change in the aniline point curve with decreasing pill size is obtained in prehydrogenation with them, the present disadvantage of K 8376, against K 5058, of a higher aniline point of the gasoline and a lower aniline point of the middle oil, particularly in the higher fractions, with equal aniline point of the total prehydrogenation product, could be overcome by conversion to smaller pills. Experiments with the pilled DHD catalyst K 7935 have already

produced this result, that the smaller pills have the effect of considerably retarding the deterioration of the catalyst and, therefore, increasing the length of the cycle, wherewith the previous disadvantage of the pilled DHD catalyst against the lumpy on Oppau alumina, K-7360, is probably eliminated. The conversion to smaller pills has already been prepared in the catalyst factory.

/pkl

TABLE 1

FEED OILS (Ausgangsöle)

Analysis	For Benzination P-1203 (middle oil from Bruchsal Oil)	For Prehydrogenation P-1271 (Liquef. Middle oil from Scholven)
Spec. Grav./20°C	0.825	0.974
Aniline Point, °C	+66	-19.0
ASTM:		
Begin °C	175	212
% - 180°C	1.5	-
% - 200°C	7.5	-
% - 225°C	26.5	12
% - 250°C	48	37
% - 275°C	71.5	53
% - 300°C	92	80
% - 325°C	97	96.5
End Point, °C	337	332
%	98.2	99

Table 2 - CONDITIONS AND RESULTS OF EXPERIMENTS

Table 2 - con't.

	Benzination (P 1203 Mi-oil)						Prehydrogenation (P 1271)					
Pressure atm	250			250			250			250		
Temperature mV	18			19.5			(18-) 19.5			(19-) 20.5		
" °C	357			382			(357-) 382			(374-) 400		
Thruput kg/kg cat/h	0.35			0.35			0.35			0.35		
Thruput kg/ltr/h	0.80	0.97	0.70	0.80	0.97	0.70	0.80	0.97	0.70	0.80	0.97	0.70
Catalyst	10 mm Pills	3 mm Pills	2-4 mm Grains	10 mm Pills	3 mm Pills	2-4 mm Grains	10 mm Pills	3 mm Pills	2-4 mm Grains	10 mm Pills	3 mm Pills	2-4 mm Grains
Gasol. Concentr. %-180°	39.8	36.4	38.4	58.7	62.3	67.7	25.8	25.5	20.5	37.7	37.8	29.0
Gasol. Yield	0.305	0.35	0.255	0.43	0.565	0.43	0.205	0.25	0.145	0.29	0.365	0.20
Gasol. Yield/kg cat	(0.13)	(0.125)	(0.125)	(0.19)	(0.20)	(0.21)	(0.09)	(0.09)	(0.07)	(0.125)	(0.13)	(0.10)
Gasif/gasol. + Gasif.	10.4	8.0	7.5	13.7	12.5	10.7	7.2	7.1	-	7.8	9.8	12.8
% C_4 in Gas	29	28.5	40	48	44.5	57.5	V/E=2.0	V/E=2.0	-	V/E=3.1	V/E=4.1	V/E=4.2
% C_5 in Gasol.	5.1	4.9	3.6	10.0	6.8	9.8	-	-	-	-	-	-
Total Product:												
Spec. Grav/20°	0.771	0.777	0.771	0.745	0.745	0.740	0.853	0.847	0.868	0.821	0.822	0.829
Aniline Point °C	70.3	71.3	71.3	67.5	67.5	66.8	36.1	40.7	31.5	43.5	46.5	47
ASTM: % - 150°	22.9	17.8	15.5	42.3	43.0	43.3	15.3	12.5	8	25.0	21.5	19
% - 180°	39.4	34.8	35.5	61.0	64.0	67.0	23.8	24.5	18.8	39.0	35.0	29
% 250°	77.8	76.8	78.5	89.8	93.5	96	70.3	69.5	59	82.0	81.0	59
End Point °C	306/97.6	300/97.8	298/97.8	289/97.5	274/97.8	253/96.8	309/98.3	315/98	325/97.8	299/98	294/97.5	296/97.5
Gasol. - 180°: Wt.-%	40.0	35.9	38.2	58.8	61.8	67.2	25.3	25.2	20.3	37.5	37.6	28.9
Spec. Grav/20°	0.734	0.740	0.739	0.717	0.726	0.725	0.788	0.791	0.804	0.766	0.777	0.784
Aniline Point °C	61/62.4	60.5/61.3	60.8/61	62.5/63.0	62.5/62.8	62.5/63	28.3/47	24.8/45.8	11.4/44	37/50	34/48	29.5/46
ASTM: Begin °C	56	62	68	47	51	47	74	86	90	72	73	78
% - 70°	3.1	1.0	0.8	8.3	3.8	4	-	-	-	-	-	-
% - 100°	15.1	10.3	11.3	28.8	21.0	21	9.3	6	3	18.5	14	12.5
% - 120°	31.3	26.0	24.8	47.3	39.5	37.8	43.5	40.8	44	50	41	44
% - 150°	72.1	70	68.5	81.2	77.0	75.3	78.8	78.8	82	82	74	78.5
Octane Number: Res.-Meth.	49.8			54.2			70.8			67.8		
Mot.Meth./M.M. + 0.12 % Pb	51.6/79.8	-	-	55.1/83.2		-	68.3/84		-	66/86		-
Mi-oil > 180°: Wt.-%	59.7	65.7 -?	61.7	41.3	37.7	32.4	74.3	74.5	79.5	62.3	62.2	71.0
Spec.Grav/20°	0.797	0.795	0.792	0.785	0.783	0.776	0.875	0.870	0.887	0.858	0.851	0.851
Aniline Point °C	77	77.3	78	76	76.3	77	40	47	37	48.5	54.5	55
ASTM: % - 225°	35.6	37.8	39.5	54.3	67.0	77.8	30.3	30.8	19.5	44.0	41.0	39
% - 275°	82.1	84.8	88	90.7	95.5	-	84.5	85.8	81	90.5	92.0	89.5
End Point °C	311/98.5	304/98.5	300/98.8	295/98.3	284/98.5	265/98.8	312/98.5	310/98.8	322/98.5	306/98.5	301/99	305/99
Phenols	-	-	-	-	-	-	-	0.055	0.067	-	0.008	-
Gasol. - 150°: Wt. -%	25.3	20.5	24.9	39.8	44.0	42.5						
Spec. Grav./20°	0.712	0.724	0.725	0.700	0.707	0.718						
Aniline Point °C	60/61	58.5/59	60/59.5	62/62.5	62/62	61.5/62						
ASTM: Begin °C	43	53	59	41	51	49						
% - 70°	10	3	3	16	8	9						
100	38	25	25	50	37	41						
120	66	57	53	76	66	62.5						
Octane Number: Res.-Meth.	-			60.4								
Mot.Meth./M.M. +0.12 Pb	61/86	-	-	62.5/86.5	-	-						
Mi-oil >150°: Wt.-%	74.3	79.0	74.9	59.5	55.0	57						
Spec.Grav./20°	0.790	0.792	0.785	0.780	0.774	0.767						
Aniline Point °C	74.5	74.8	75	72.5	74.5	73						
ASTM: % - 200°	30	30	34	51	60	71						
250	70	72	78	84	94	96						
End Point °C	308/98	304/98.5	296/98.5	292/98	271/98.5	261/99						

/pkl

TABLE 3

Aniline Point Fractions

Form of Catalyst	10 mm - Pills			3 mm - Pills			2 - 4 mm Grains		
Date - 1943	2./3.5	3.5	4.5	13.5 10-18	13.5	14.5	24.5	25.5	26.5
Temperature mV	18/19.5	18/19.5	19/20.5	18/19.5	18/19.5	19/20.5	18/19.5	18/19.5	19/20.5
Thruput kg/ltr/h	0.80	0.80	0.80	0.97	0.97	0.97	0.70	0.70	0.70
Gasol.Concentration %-180°	27.7	23.8	37.7	26.0	25.0	37.8	-	20.5	29.0
Total Product:									
Spec. Grav/20°	0.845	0.860	0.821	0.845	0.849	0.822	0.865	0.870	0.829
Aniline Point °C	37.0	35.2	43.5	40.5	40.8	+46.5	+32	+31	+47
A.P. - 180°	31.5	27.5	38.0	28.0	26.5	35.5	-	16	30
>180°	40.0	38.5	40.0	43.5	44.2	51.0	-	33	52
ASTM: Begin °C	93	100	69	107	103	93	105	110	82
% - 100°	1.0	-	3.0	-	-	2	-	-	2
150	18.0	12.5	25.0	13	12	21.5	9	7	19
180	28.0	19.5	39.0	25	25	35.0	18.5	19	29
250	73.0	67.5	82.0	70	69	81.0	58.0	60	59
End Point °C	302/98.0	315/98.5	299/98.0	312/98	318/98	294/97.5	322/97.5	325/98	296/97.5
A.P. Fractions:									
-100° Wt.-%	5.7	2.4	7.9	2.5	3.8	6.7	3.1		6.3
Sp. Grav./20°	0.750	0.761	0.725	0.747	0.767	0.734	0.780		0.756
A.P.	31.0	27.0	39.5	27.5	21.5	35.0	11.0		27
100-120°								-120	
Wt.-%	6.0	5.1	9.0	9.5	6.8	9.5	5.0	4.2	6.1
Sp. Grav./20°	0.775	0.778	0.765	0.780	0.788	0.768	0.792	0.786	0.775
A.P.	28.0	24.0	34.0	22.0	23.5	29.5	10.5	13	25
120-140°									
Wt.-%	4.9	6.1	5.3	2.8	6.6	5.9	4.5	5.0	4.0
Sp. Grav./20°	0.785	0.738	0.776	0.791	0.800	0.780	0.802	0.804	0.798
A.P.	29.0	26.0	36.0	23.0	24.0	31.5	8.5	11.5	33
140-160°									
Wt.-%	5.2	4.2	5.9	6.3	4.0	4.4	3.4	5.8	10.7
Sp. Grav./20°	0.806	0.802	0.788	0.806	0.812	0.795	0.815	0.818	0.800
A.P.	30.5	27.5	38.0	26.5	26.0	35.5	9.0	11.5	33
160-180°									
Wt.-%	6.3	4.0	7.6	3.4	3.8	7.5	4.1	6.7	2.8
Sp. Grav./20°	0.821	0.822	0.805	0.824	0.830	0.808	0.829	0.833	0.815
A.P.	32.0	28.0	40.0	30.0	30.5	39.0	15.5	15	43
180-200°									
Wt.-%	7.8	7.3	12.8	7.8	10.2	10.5	7.1	4.1	9.0
Sp. Grav./20°	0.840	0.843	0.826	0.838	0.846	0.824	0.849	0.849	0.825
A.P.	33.0	30.5	41.5	34.0	34.5	43.0	21.0	18	44
220-225°									
Wt.-%	17.2	20.5	14.7	17.7	16.0	18.5	12.3	15.5	19.3
Sp. Grav./20°	0.860	0.859	0.842	0.855	0.859	0.836	0.867	0.868	0.840
A.P.	36.0	33.0	44.0	38.0	38.5	47.5	24.5	24.8	48
225-250°									
Wt.-%	16.8	10.3	13.6	16.9	16.0	13.7	18.0	17.4	18.1
Spec. Grav./20°	0.870	0.873	0.858	0.866	0.868	0.850	0.879	0.884	0.852
A.P.	39.0	37.0	48.0	44.0	45.0	54.0	33	30.8	55
250-275°									
Wt.-%	17.5	22.1	14.3	19.4	18.5	17.5	16.2	19.3	17.1
Sp. Grav./20°	0.885	0.836	0.872	0.880	0.884	0.861	0.889	0.893	0.863
A.P.	44.0	42.5	52.0	51.0	50.8	59.5	40.0	38.5	60
>275° (275-300)									
Wt.-%	13.0	11.9	7.3	8.3	14.2	5.0	19.7	16.8	6.0
Sp. Grav./20°	0.900	0.900	0.895	0.886	0.890	0.865	0.900	0.904	0.860
A.P.	49.0	45.0	57.0	60.0	59.5	67.0	48.5	45.0	71
>300°									
Wt.-%		5.4					5.5	5.0	
Sp. Grav./20°		0.922					0.902	0.904	
A.P.		53.5					63.5	57.0	
Loss %	0.5	0.7		1.4	0.1	0.8	1.1	0.2	0.6

T-322
Table 3
con't

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T-323

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

PRESSURE HYDROGENATION OF DRY COAL

By Donath & Rotter, Ludwigshafen, 29 Jan. 1943.

The purpose of the experiments is to determine if an appreciable oil yield can still be obtained in the hydrogenation of coal at moderate pressures, e.g. 10 to 50 atm. Hydrogenation of coal in powdered form, without pasting oil, appears technically possible at such pressures. Compare, e.g., pressure gasification. In order to obtain preliminary figures, experiments were made in a tray autoclave without pasting oil and, at first, without catalyst.

For the time being, some data on Rhenish brown coal (68.7% C) and Upper Silesian bituminous coal (78.9% C) are available. The figures obtained are contained in Table 1. The most important data for brown coal dependent upon temperature are given in Figure 1 and those dependent upon pressure in Figure 2. Figure 3 shows these values for bituminous coal dependent upon pressure.

In detail, brown coal shows an increase in conversion and oil yield when the temperature is increased from 22 to 25 mV, while gasification apparently is a maximum at about 24 mV, determined solely by the apparatus. Oil yield and pure coal conversion naturally increase with increasing pressure. A distinct minimum in gasification, previously unknown, at a pressure of about 25-50 atm. is, however, worthy of note. The dependence upon pressure is similar for bituminous coal, although at 25-50 atm. the oil yield is lower than for brown coal.

The following detailed data were obtained for brown coal at 25 mV:

Pressure	0	10	25	50	230
% pure coal conversion	45	53	59	65	84
% oil yield/pure coal	8	15	23	30	47
% gasif./oil yield + gasif.	42	34	28	25	32
% H-C gasif./oil yield + H-C gasif	(36)	24	19	16	28
% C as CO + CO_2 in gasification	-	-	(40)	(40)	(20)

The comparatively high oil yield and low gasification at 25-50 atm. appear to make such an operating method promising, if it is possible to avoid processing the residue. This appears possible in a simple manner by separating the oil produced in vapor form with the H_2 from the pulverized converted coal. It should be noted that only in the experiments at 230 atm. did this residue occur in melted, blistered coke-like form. An apparatus for semi-continuous operation of this process is being built.

Table 1.

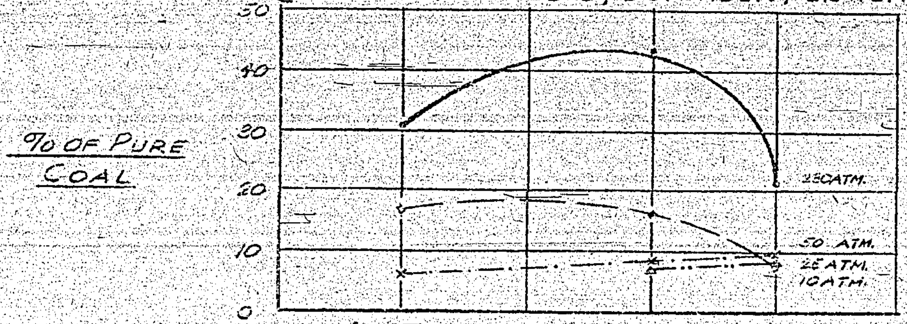
Pressure Hydrogenation of Brown and Bituminous Coal in Tray Autoclave

	Conditions of Experiments													
	H_2 Press. atm.	Temp. mV.	Gas Ltr/h	Per Cent Raw Yield (Output/Input)	Per Cent Pure Coal Conversion/ Solids	Oil + Light Ends /Pure Coal	Gasif. Pure Coal	Gasif./ Oil + Gasif. (with light ends)	H-C Gasif. /Oil + H-C Gasif.	% CO_2+CO in Gas	Spec. Grav. of Oil/ 20°C (without light ends)	% Asphalt in Oil (without light ends)	Boiling Curve %-200°	Boiling Curve %-350°
Rhenish Brown Coal (K 229 v.30.6.42)	230	22(426°C)	600	107.0	78.0	42.8	31.5	42.4	40.4	8	0.957	Trace	-	-
H_2 O - 6.4%	230	24(460°C)	600	98.5	86.0	44.8	43.2	49.1	47.5	6	0.966	"	-	-
Water-free Coal Ash 5.4%	230	25(476°C)	600	101.3	87.-	46.7	22.2	32.2	28.0	18	0.987	"	-	-
Pure Coal: C 68.7% H 5.1"	50	22	150	99.6	55.8	27.0	17.5	40.2	32.0	30	0.962	0.7	12	78
O 24.9" N 1.3"	50	24	150	98.6	61.1	24.8	16.4	39.8	39.0		0.969	Trace	-	-
S 0.4"	50	25	150	84.3	68.5	30.0	8.6	25.6	14.7	43	0.961	0.9	19	79
Crude Tar 11.25%	25	22	75	87.0	51.0	19.5	6.2	24.2	11.0	61	0.970	0.7	-	-
	25	24	75	87.5	59.5	21.0	8.9	28.9	21.0	33	0.970	0.9	0	57
	25	25	75	91.0	61.2	22.8	9.1	28.6	19.0	41	0.935	0.8	10	72
	10	24	50	86.3	55.4	11.9	7.0	37.1	21.5	54	0.968	1.3	-	-
	10	25	50	100.0	58.7	27.2	9.1	25.0	22.6	13	0.926	1.7	0	57
	0	26	25	96.3	44.4	7.0	5.1	42.2	36.0	22	-	-	-	-
Upp.Sil.Bit.Coal (K-1251 v.31.7.42) H_2 O - 1.2%	230	25	750	94.0	67.8	32.0	14.1	35.2	28.6	9	1.014	1.1	17	62
Water-free Coal Ash 4.6%	50	25	150	96.5	57.7	14.7	5.9	28.3	22.6	32	1.050	-	0	60
Pure Coal: C 78.9%	25	25	75	98.4	33.8	15.3	5.9	27.7	22.0	27	1.042	2.0	-	-
H 4.9" O 14.4" N 1.3 S 0.6 Crude Tar 8.4	10	25	50	98.7	29.2	7.9	5.6	41.7	43.7	-	1.082	-	-	-

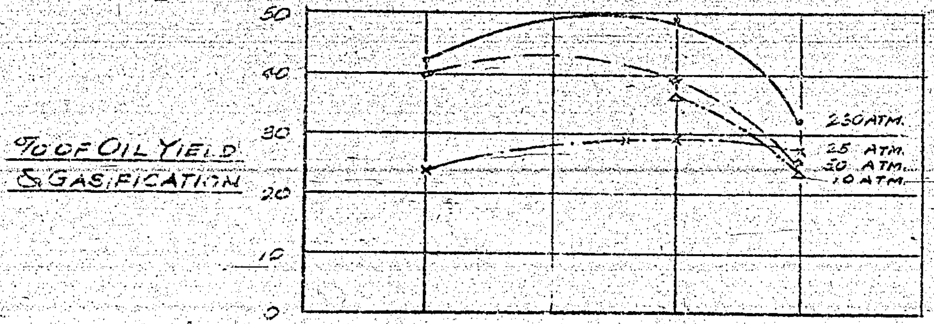
Conditions of Experiments: (After dipping the tray autoclave into the preheated lead bath, the gas analyses were made.
Length of experiment: each 4 hrs. on temperature.
Length of preheat.: each 1 hr.

T-323
FIG. 1

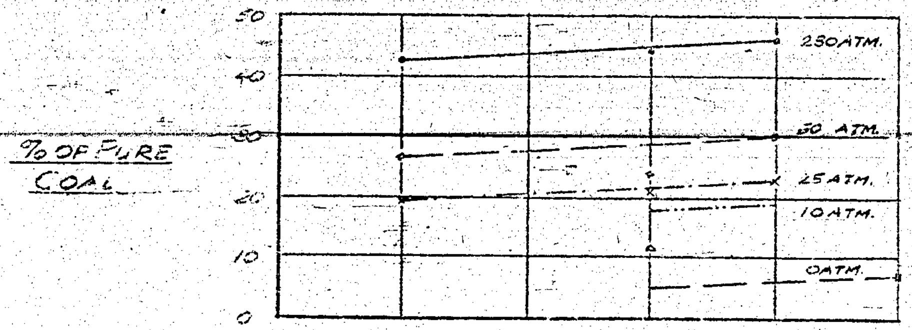
PRESSURE HYDROGENATION OF BROWN COAL
(K 229 RHEIN BR. COAL, DEPENDENT ON TEMP.)



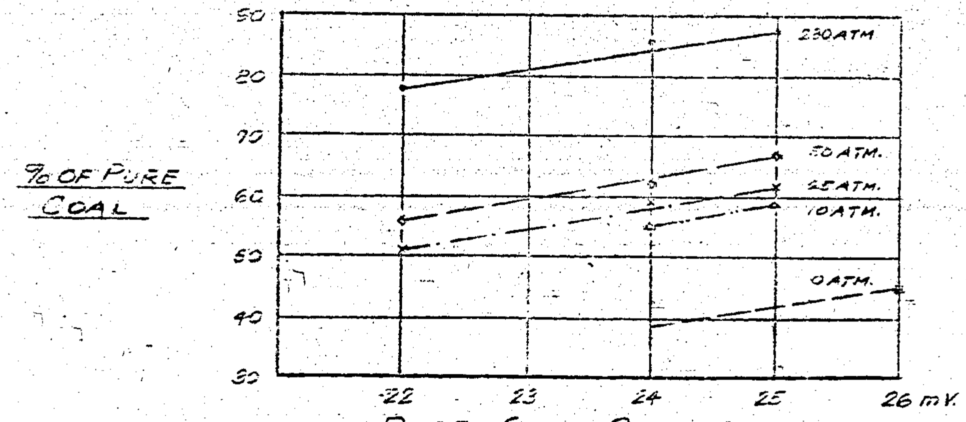
TOTAL GASIFICATION



TOTAL GASIFICATION



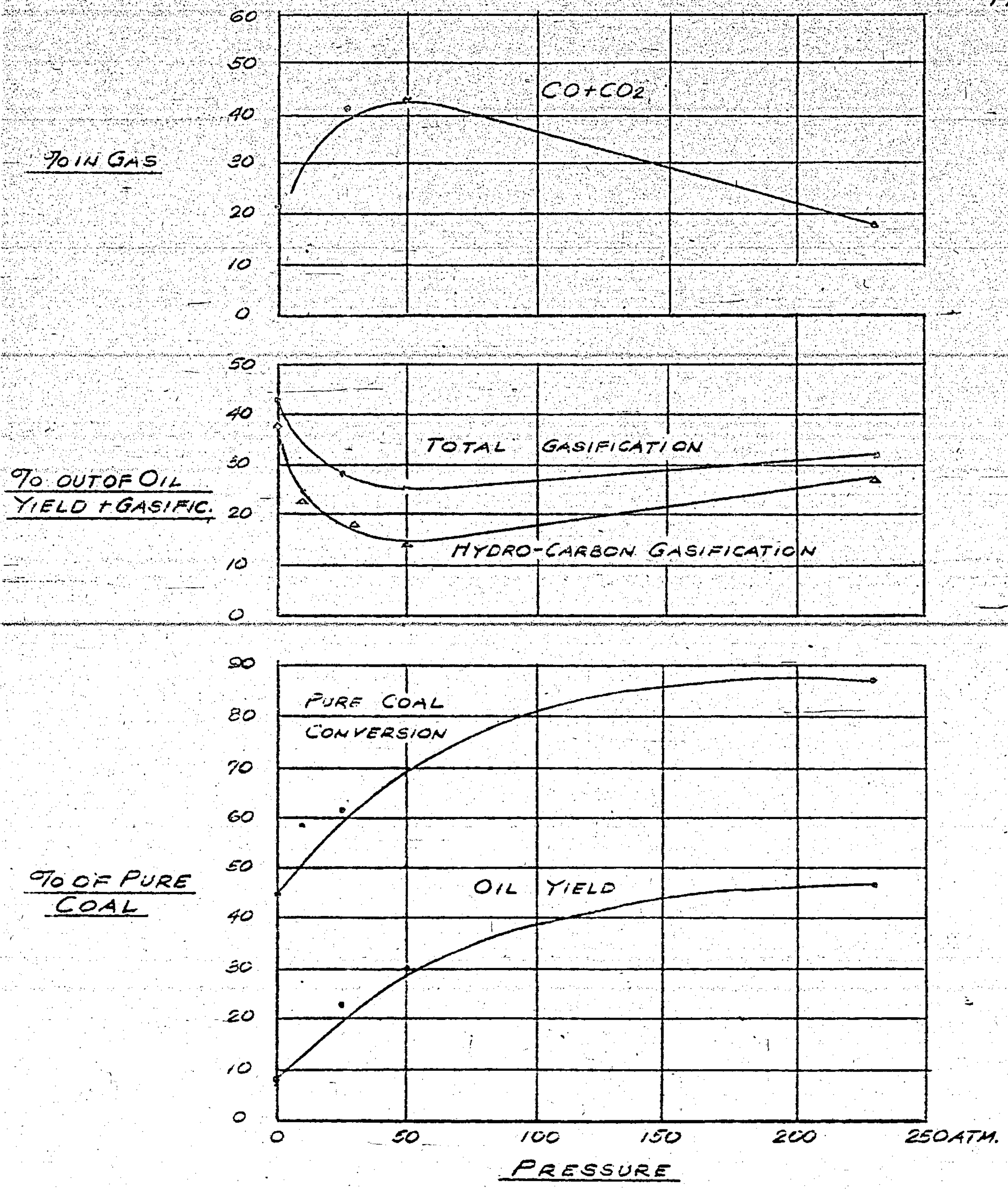
OIL YIELD



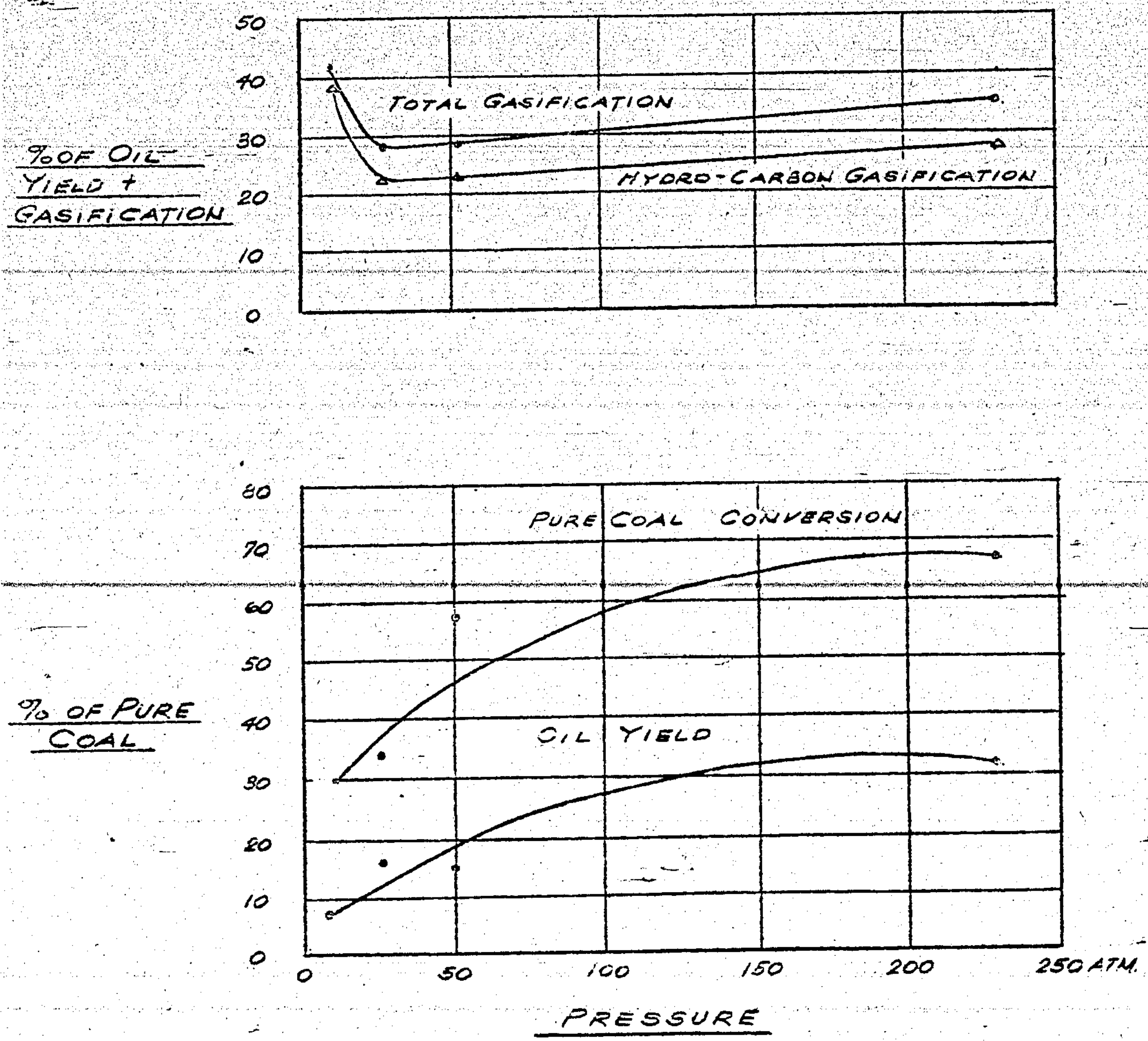
PURE COAL CONVERSION

T-323
FIG. 2

PRESSURE HYDROGENATION OF BROWN COAL
(K229 RHEN. BR. COAL)
DEPENDENT UPON PRESSURE @ 25 in V (476°C)



PRESSURE HYDROGENATION OF BITUMINOUS COAL
(K-1252 UPP. SIL. BIT COAL)
DEPENDENT UPON PRESSURE @ 25 m.V (476°C)



751 T-324
W.M. Sternberg

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

From Dr. M. Pier's private files.

4 PAPERS ON CONTRIBUTIONS ON THE LIQUID PHASE IN

"Oel and Kohle"

Properties of Hydrogenation Products from Various Raw Materials

I. 11-9-42

OLD BITUMINOUS COAL (RUHR)

	g ash 100 g coal	g H 100 g coal	g O+N+S 100 g coal
Coal	(?)	6.0	9.0
Extract	0.06	6.3	6.9
Heaviest oil	-	7.9	4.3
Liquid phase distillation heavy oil	-	8.9	1.7
Liquid phase middle oil	-	11.0	2.4
Vapor phase middle oil	-	15.0	-
Gasoline	-	16.9	-

YOUNG BITUMINOUS COAL (RUHR)

	g ash 100 g coal	g H 100 g coal	g O+N+S 100 g coal
Coal	5.0	6.4	14.2
Extract	0.1	7.0	9.5
Heaviest oil	-	8.4	4.4
Liquid phase distillation heavy oil	-	9.3	2.8
Liquid phase middle oil	-	10.9	4.8
Vapor phase middle oil	-	15.0	0
Gasoline	-	17.0	0

LOW BITUMEN BROWN COAL

	g ash 100 g coal	g H 100 g coal	g O+N+S 100 g coal
Coal	9.6	7.1	38.4
Extract	-	7.8 - 8.1	6.4 - 7.3
Heaviest oil	-	8.9	3.4
Liquid phase distillation heavy oil	-	9.5	3.4
Liquid phase middle oil	-	11.4	5.4
Vapor phase middle oil	-	15.2	0
Gasoline	-	17.3	0

HIGH BITUMEN BROWN COAL

Coal	18.0	8.5	33.5
Extract	0.7	8.7	13.2
Heaviest oil	-	9.0	4.5
Liquid phase distillation heavy oil	-	10.2	1.6
Liquid phase middle oil	-	12.0	4.5
Vapor phase middle oil	-	15.5	0
Gasoline	-	17.6	0

ASPHALTIC BASE MINERAL OIL.

Mineral oil residue	-	12.2	7.2
Heaviest oil	-	10.3	2.8
Liquid phase distillation heavy oil	-	11.3	2.7
Liquid phase middle oil	-	13.7	1.7
Vapor phase middle oil	-	16.0	0
Gasoline	-	17.7	0

	g per 100 g.C	Old bituminous coal (Ruhr)	Young bituminous coal (Ruhr)	Low bitumen brown coal	High bitumen brown coal	Asphaltic base mineral oil residue
Raw material	Ash	5.0	5.0	9.6	18.0	-
	H	6.0	6.4	7.1	8.5	12.2
	O+N+S	9.0	14.2	38.4	33.5	7.2
Extract	Ash	0.06	0.1		0.7	
	H	6.3	7.0	7.4 - 8.1	8.7	
	O+N+S	6.9	9.5	6.4 - 7.3	13.2	
Heaviest oil	H	7.9	8.4	8.9	9.0	10.3
	O+N+S	4.3	4.4 ?	3.4 ?	4.5	2.8
Liquid phase dist. heavy oil.	H	8.9	9.3	9.5	10.2	11.3
	O+N+S	1.7	2.8	3.4	1.6	2.7
Liquid phase middle oil	H	11.0	10.9	11.4	12.0	13.7
	O+N+S	2.4	4.8	5.4	4.5	1.1
Vapor phase middle oil	H	15.0	15.0	15.2	15.5	16.0
	O+N+S	-	-	-	-	-
Gasoline	H	16.9	17.0	17.3	17.6	17.7
	O+N+S	-	-	-	-	-

II

Nov. 9, 1942

ON THE CONCEPTIONS OF BITUMEN AND ASPHALT

In the industrial as well as scientific nomenclature there existed much contradiction in the terms for tar and pitch. Mallison's subdivision of the concepts for bitumen in 1933 are still used today:

I. Bitumens (natural products)

- A. Mostly soluble in CS_2 and saponifiable
  (sapropels, Montana wax, fossil resins)
- B. Mostly soluble in CS_2 and unsaponifiable
  - 1. ozokerite
  - 2. Mineral oils and their distillation residues
    - a) liquid
      - a-1 Paraffin base mineral oil
      - a-2 Mixed base mineral oil
      - a-3 Asphaltic base mineral oil
    - b) Semi-liquid or solid, fusible
      - b-1 Paraffinic mineral oil residues
      - b-2 Paraffinic-asphaltic mineral oil residues
      - b-3 Asphaltic mineral oil residues
- C. Mostly insoluble in CS_2, unsaponifiable
  (elaterite, peat, brown coal, oil shale)

II. Substances Related to Bitumens.

- A. Tars and Pitches (obtained artifically by destructive distillation of natural organic substances) (In the distillation of tar oils, the residues: tar pitch)
  - 1. Tars
    - a) Wood tar
      - a-1 Sedimentation tar
      - a-2 Retort tar
    - b) Peat tar
    - c) brown coal tar
    - d) Shale tar
    - e) Bituminous coal tar

f) oil gas and water gas tars

g) Tars from fats

h) Bone tar

2. Pitches:

a) distillation residues from tar

b) Carbolic and naphtholic pitches

c) Resin pitch

d) Montana wax pitch.

B. Refinery residues (obtained by chemical treatment of bitumens, tars and pitches)

Acid resins.

Presumably, all the naturally occurring substances, or products obtained from natural products without decomposition and consisting of hydrocarbons, must be called bitumens. This arrangement is largely in agreement with that used in the German scientific work and the usual American way. The difficulty existing in Germany of calling bitumen the distillation residues of asphaltic base mineral oils is overcome by calling also the CS_2-soluble components of natural asphalts bitumens in the narrower meaning of the word. In other words, the wider meaning of the term, bitumens are the substances enumerated in the table, while in the narrower, practical meaning bitumens are the distillation residues of asphaltic base mineral oils.

In Germany the term asphalt means the natural or artificially produced mixture of bitumen in the narrower meaning of the term with mineral substances in varying proportion. The word asphalt should not be used for pure soluble bitumens.

A term like mineral oil asphalt must therefore be avoided. In America, bitumen in the narrow sense is called asphalt.

We understand by tar the liquid and semi-liquid products of thermal decomposition of natural organic substances, such as peat, wood, brown or bituminous coal, obtained as byproducts. Pitch is the distillation residue of tars.

Gas-und Wasserfach, vol. 83, 1940, p. 241)

E. J. Fischer distinguishes between

I. Natural asphalts

II. Artificial asphalts and pitches

a) mineral oil residues

b) tar pitch (distillation residues of tars)

c) direct pitch (direct residue of drydistillation)

III. Chemoasphalts and Chemopitches (asphalt or pitchlike materials obtained chemically either directly, or as a residue of distillation of asphalts, mineral oil residues, tars, etc.)

Products obtained by the hydrogenation of asphalts, pitches, tars, tar oils, etc, are to be put into this third group.

(Die natürlichen and künstlichen Asphalte und Peche, 1928)

signed: Henkels

III Nov. 7, 1942

PARALLELS BETWEEN THE THEORIES OF FORMATION OF NATURAL BITUMENS AND THE PRODUCTS OBTAINED IN PRESSURE HYDROGENATION

The theories of formation of mineral oils, asphalts, resins and coal, based on the effects of high pressures and temperatures during geologic ages upon plant and animal raw materials, are of certain significance in the scientific study of pressure hydrogenation, especially in the liquid phase. Many investigators have assumed a catalytic action of several minerals, among which the bituminous raw materials were dispersed more or less intimately. Occasionally, the action of gaseous hydrogen was also considered in this connection. Certain parallels may therefore be drawn between these processes and what happens in the liquid phase or in processes at elevated temperatures and under pressure. The polymerization of asphaltic-base mineral oils to asphalts under the influence of high pressures at high temperatures, as well as splitting, depolymerization and dehydrogenation, are transformations which occur during pressure hydrogenation and pressure extraction. The presence of hydrogen or of substances giving off hydrogen, possibly with catalysts, change the transformation products originally formed at the high temperatures and pressures. Gaseous, liquid and solid hydrocarbons of greatly different molecular magnitudes such as asphaltides, waxes, etc, exist side by side in natural deposits as they do in the products of pressure hydrogenation. Depending on the chosen conditions and catalysts, pressure hydrogenation permits on the one side the production of the most diversified groups of hydrocarbons from one raw material, as well as preferential production and isolation of certain types present in the raw material. The final products of the liquid phase hydrogenation still permit the recognition of specific properties of the raw materials. The generic differences of the bitumens are at times more pronounced in the final products of the liquid phase than in the original raw material. This in turn permits us to draw conclusions on the origin of the raw materials, so that the development and application of pressure hydrogenation represents a valuable supplement and elaboration of other investigation methods. Thus, a pressure extraction under mildly hydrogenating conditions permits an almost complete transformation of the infusible organic coal matter into fusible and soluble bitumens, which possess characteristic differences depending on the nature of the coal hydrogenated and are more strongly differentiated than the mineral oil asphalts and asphaltites. The brown coal produced from the more highly organized plants rich in resins and waxes produces a bitumen, which breaks down upon melting into a waxy paraffinic portion and a lower-hydrogen asphaltic-portion. Bituminous coals formed principally from lower cryptogams produce more uniform extracts, relatively low in hydrogen and more similar to the asphaltic portion from the brown coal. The older a coal, the lower is the hydrogen content of its extract. The solubility behavior of the coal extracts, especially in mineral oil asphalts, is another difference. The destructive hydrogenation of coal in the liquid phase produces during simultaneous hydrogenation and dehydrogenation some undefined mixtures of resins and asphalts, and also some well defined and well crystallized ring systems, which are particularly resistant under the conditions used because of their constitution. The investigation of such groups of substances and their transformation products may result in valuable conclusion on chemical configuration of the carbonaceous substance and its formation from the plant raw material.

/s/ Rank

ASPHALTS OF DIFFERENT ORIGIN

	Natural asphalt (Trinidad)	Asphaltite (Bentheim)	Boghead coal (Ruhr)	Bituminous coal extract (Ruhr)	Brown coal extract Central Germany
Softening point	87°	Does not melt undecomposed.		210°	70-100°
Ultimate analysis of the pure sample					
%C	81	87.65	80.08	88.91	82.28
%H	10.5	9.05	8.90	5.53	6.85
%O	0.8	1.73	6.01	3.30	8.01
%N	0.7	1.29	1.71	1.70	0.98
%S	7	0.28	3.30	0.56	1.78
g H/100 C	13.0	10.3	11.1	6.2	8.3
g (O+N+S)/100 g C	10.5	3.8	13.7	6.2	13.1

IV.

Nov. 14, 1942

LIQUID PHASE ASPHALTS

The liquid phase raw materials are primarily mixtures of different high-molecular weight raw materials, such as mineral oil, tar residues, coals, etc. Liquid phase pressure hydrogenation produces from the low and middle-molecular weight substances, such as gasoline and middle oils, as well as heavy oils, heaviest oils and asphalts, which in turn may lead to a continuous transition to the so-called solid organicals. While there is at present no direct use for these high molecular weight compounds, they are freed as thoroughly as possible from ash and solids, and returned to the process as pasting oils for further hydrogenation and splitting. Finally, a small part of these heaviest oils which stays with the ash and the solids is kilned.

An investigation of the high molecular weight products of hydrogenation meets considerable difficulties, of the same nature as the investigation of the naturally occurring high molecular compounds. True solutions, colloidal and coarse dispersions exist side by side, and affect each other during chemical or physical investigations. For this reason the properties of such substances separated from the mixtures by any of the available methods are greatly affected by the impurities present in them. However, the application of the method of decomposition with solvents and adsorbents into separate groups of substances of high molecular weight, used in the mineral oil and tar industries, give valuable information on the high molecular weight compounds obtained in hydrogenation. One may follow in such decomposition of the high molecular group substances the connection between the raw materials and the hydrogenation products obtained from them, as well as the effects of varying hydrogenation conditions upon the same raw material. The high molecular weight substances from the heaviest hydrogenated petroleum oils have a different composition than the corresponding products from coals and tars, and the different mineral oils, tars and coals give different high molecular weight systems. These substances must be considered as the primary splitting and hydrogenation products from the raw materials, and they are therefore of particular interest. The liquid phase hydrogenation attacks the structure of the natural high molecular weight compounds very sparingly in comparison with the crude thermal methods of cracking, low or high temperature coking. Liquid phase hydrogenation converts almost all the combined coal material into liquid and soluble substances, while in the high and low temperature coking only a small part of the material is attacked, namely the so-called bitumens. The principal high molecular weight substances obtained in hydrogenation are therefore preferentially capable of throwing light upon the constitution of the starting material.

A number of interesting facts could as a result be learned about the appearance of highly condensed aromatic ring systems in the hydrogenation asphalts. The different ring systems possess different stability against the splitting, hydrogenation and dehydrogenation reactions which occur simultaneously during the destructive hydrogenation. The continuous return of the high molecular weight substances into the process may especially enrich the most stable ring systems. Highly condensed aromatics and hydroaromatics have been obtained only in very limited amounts from the asphalts, resins or heavy oils from hydrogenation but the structure of these aromatics may never-the-less permit drawing conclusions on the configuration of the hydrogenation asphalts, especially because these aromatics exhibit practically the same reactions with different substances, as do the asphalt systems themselves. The particularly symmetrically constructed coronene has so far been identified in hydrogenation asphalts from different raw materials, as well as pyrene, its homologues and benzopryenene. There are also indications of transitions from the amorphous asphalts to these crystalline aromatics. The present status of investigations does not, however, permit us to state whether these ring systems are present in the original raw material, or are formed during the destructive hydrogenation from the primary splitting residues.

/s/ Rank

Ultimate Analysis of Liquid Phase Asphalts from the HOLD of Various Hydrogenation Works

	Gelsenberg	Pölitz	Ludwigsh.	Scholven	Rheinbraun
% C	88.90	89.79	90.33	92.06	87.
% H	4.83	4.31	4.93	4.39	7.
% O	3.85	3.64	2.99	2.13	3.
% N	2.21	1.74	1.66	1.35	0.
% S	0.21	0.02	0.09	0.07	0.
g H 100 g C	5.42	5.35	.45	4.76	8.
g O+N+S 100 g C	7.05	6.0	5.24	3.85	5.68

Practically Asphalt-Free Heavy Oils (Init. boil. pt. 350°)

	Bitumin. coal	Brown coal	Mineral Oil		Lubricat. oil
			H-poor	H-rich	
sp.gr., 20°C	1.068	0.980	0.964	0.905	0.882
Viscos., °E, 50°C	18.3	8	82	11	17.4
% C	89.2	88.0	86.91	86.33	86.23
% H	8.2	9.7	11.35	12.60	13.36
% O	1.7	0.9	1.30	0.30	0.34
% N	0.86	0.6	0.05	0.01	0
% S	0.04	0.8	0.39	0.26	0.07
g h 100 g C	9.2	11.0	13.1	14.5	15.49
g O+N+S 100 g C	2.9	2.6	2.0	0.65	0.47

/pkl

U. S. BUREAU OF MINES T-325
HYDRO. DEMON. PLANT DIV.

KCBraun
4-17-47

Turbo-Precompressors in Hydrogenation Plants, With Particular Reference to the Demand for Economy in Construction Materials

(Lecture by Mr. Wanser of the "Mineralöl-
Baugesellschaft" in the Reichs-Office for
Industrial Expansion on March 3, 1943, in Berlin)

I. - The compression of large quantities of gas from atmospheric pressure to moderate final pressures is, without a doubt, the province of the turbo-compressor. Under such conditions the efficiency of the turbo-compressor equals that of the piston compressor, so that the question of an economic drive need not be considered in detail, although this is of decisive importance for the use or non-use of turbo precompression in special cases, such as in hydrogenation plants.

That turbo precompression has not found practical application in domestic hydrogenation plants was not because we couldn't build suitable machines for this purpose, but entirely because of the drive problem. The direct electric drive with high tension squirrel cage motor was considered the most suitable, because of its simplicity and cleanliness, but was at such a disadvantage because it required 3.5 times the normal starting current, that, for that reason alone, turbo-compressors of economically large capacities could never be used.

Therefore, turbo precompression with direct motor drive as with other machines in hydrogenation could never hold its own.

However, the advantages of turbo precompression are so great that the use of this method of compression can not be made dependent upon the electric drive alone. Even though the thermal efficiency of the turbo compressor with the light gas mixtures to be conveyed is below that of the piston compressor, and a correspondingly greater capacity requirement (Leistungsbedarf) must be allowed for, this is not decisive, because the greater capacity requirement of direct steam turbine driven compressors is amply covered by the elimination of the electrical losses, herebefore made allowance for, in the generator, transformer, cable and motor, with the customary electrical drives of piston compressors. It is, therefore, entirely immaterial how great the individual losses in the various machines and apparatus are, as long as the total loss does not exceed that formerly allowed for. In other words, when trying to decide for or against turbo precompression, the determining factor is not only the greater capacity requirement of the turbo compressor, but the power required for the entire gas compression, which must be delivered at the shaft of the steam turbines in the power plant.

If we look at the problem from this angle, there is probably nothing in the way of using turbo precompressors in most cases.

II. - When turbo compression is used, the gas mixture of H_2, CO, CO_2 and steam, formerly compressed in the low pressure stages of the piston compressor, must be brought to the CO_2 washout pressure in direct driven turbo compressors developed for this purpose. A washout pressure of 28 atm has been prevalent to date in a process with pressureless conversion, compared to 13 atm in a process with pressure conversion. The latter, considerably lower, washout pressure is not due to a demand for economical compression of the raw gas by means of turbo compressors, but is determined by the pressure conversion plant itself. In such a process turbo precompression is desirable, inasmuch as the gas mixture to be conveyed remains completely free of oil and no gradual deterioration of the effectiveness of the catalyst due to oil coating can occur in pressure conversion.

After freeing the raw gases of CO_2, further compression to 325 or 725 atm is done in piston compressors, as formerly.

In order to summarize the problem in figures, the following comparison between 2 H_2-pressure processes with and without turbo precompression has been worked out:

A) Pressureless Conversion: 1. without turbo precompression
2. with " "

B) Pressure Conversion: 1. without turbo precompression
2. with " "

(See Diag. 1)

Total quantity conveyed = 100000 Nm^3/h H_2(98%) @ 700 atm
Washout pressure for CO_2 = 13 atm

The gas figures given correspond approximately to the proposed Blechhammer plant, extension 1.

Diag. 2 shows the type of construction, size and number of compressors required, as well as necessary building volume and built-up floor space. It is computed from the quantities to be conveyed, determined by Dr. Pirzer of the nitrogen plant at Oppau by accurate line measurements.

Accordingly, the following are required for the cases given:

A1: - 11+2 6-stage compressors, 1-325 atm.
10+2 booster compressors, 300-725 atm.
Bldg. vol: 101800 m^3
Floor space: 7800 m^2 (built-up)

A2: - 3+1 turbo compressors, 1-13 atm.
8+2 piston compressors, 11 to 725 atm
(Special construction)
Bldg. vol: 87500 m^3
Floor space: 5550 m^2 (built-up)

B3: - 9+2 6-stage compressors, 1-325 atm.
10+2 booster compressors, 300-725 atm.
Bldg. vol: 90300 m^3
Floor space: 7000 m^2 (built-up)

B4: - 3+1 turbo compressors, 1-13 atm.
8+2 piston compressors, 11 to 725 atm.
(special construction)
Bldg. Vol: 83900 m^3
Floor space: 5350 m^2 (built-up)

It should be noted that the special piston compressors have already been developed for Blechhammer. These machines can also be run without the highest pressure stage 5. The final pressure in that case is only 325 atm. absolute.

When turbo precompressors are used, the booster compressors, developed as additional machines, besides the first 2 low pressure stages of the 6-stage compressors, are eliminated, which saves considerable building volume. By the elimination of a 20000 KW turbo-generator, no longer required, an additional building volume of 16 x 22 x 21 = 7400 m^3 is saved in the power plant, i.e. the figures in Diag. 2 are reduced by this amount, as explained below:

A2: - Ultimate Bldg. Vol: 87500 - 7400 = 80100 m^3
B4: - " " " : 83900 - 7400 = 76500 m^3

The following building volume relations then exist:

with pressureless conversion, 101800:80100
" pressure " , 90300:76500

Similar relations exist between the weights of the machines.

Diag. 3 shows the most important data for further evaluation, e.g.:

a). Power data
b). Machine personnel
c). Finished machine weights
d). Net machine costs (without installation)
e). Operating costs (without capital burden & repairs)

a). Power.

Although the capacity required at the compressor shaft for the total compression from 1 to 725 atm has increased with the use of turbo precompressors, the power plant turbine capacity is not exceeded. (See also Diag. 4, Fig. 1) The losses herebefore charged against direct electric drives are now also conceded the turbo compressors. Consequently, no increase in losses occurs, but simply a rearrangement. The considerable reduction in lubricating oil requirement with the use of turbo precompressors should also be noted. (See also Diag. 4, Fig. 3)

b). Machine Personnel.

The turbo precompressor, of course, also permits savings in labor without considering the fact that turbo compressors belong to that type of machines which are very seldom out of commission due to damages to the machine since sources of failure, e.g. valve plates and springs, piston rings, etc. are not present. The same thing, of course, also applies to steam turbines for drives.

c). Finished Machine Weights.

The use of construction materials is reduced considerably with the use of turbo precompressors. It is not only necessary to complete a job with the least possible construction material in times of material shortages, but also in the future when labor may be scarcer than materials, because each pound of steel, even unfinished, represents a part of human labor, as well as a considerablo proportion of coal necessary to produce it. If, from these points of view, we consider the saving of roughly 1200 tons of finished machine weight, turbo precompressors are the logical choice for this reason also. If we further consider that by eliminating a 20000 kwh turbo-generator we will save an additional 200 tons of finished machine weight, and that considerable quantities of copper, lead and aluminum for motors, switch gear, cables, etc., otherwise required, are released for other purposes, such as air and gas decomposition, the saving is increased to 1400 tons of finished machine weight (and much more in raw materials).

d). Net Machine Costs.

The foregoing necessarily implies reduced building costs of compressor plants in which turbo compressors are used for initial partial compression. (See also Diag. 4, Fig. 7).

e). Operating Costs.

Savings may also be obtained in this item, even if capital burden and repairs are not considered. If we consider both of these factors, turbo compression is a still better deal.

III. - Results.

The compression of light gas mixtures from 1 to 13 atm is not economical if the direct electric drive is used. However, if the steam turbine is used as direct drive, the lower thermal efficiency of the turbo-compressor, compared to the piston compressor, is fully offset by the elimination of all former electrical losses. The power plant capacity is not increased, rather decreased, therewith; consequently, there is nothing in the way of using turbo-compressors with steam turbine drive.

IV. - Outlook.

On the basis of the foregoing investigation, one may conclude that in many cases turbo compressors could even be used for processes in which CO_2 must be washed out at a pressure of 28 atm even if the power plant capacity would have to be moderately increased.

Example:

Compression of 160000 Nm^3/h = 190000 m^3/h from 1 atm to 28 atm absolute in the first 3 stages of the 6-stage piston compressor. Isothermal capacity required for 1 $m^3/min.$ = 7.4 PS (metric HP).

Nis = (190000/60) x 7.4 = 23400 PS (isothermal capacity req'd.)
Isothermal efficiency Eis = 0.69
Effective capacity req'd. Ne = 23400/0.69
= 33900 PSe
= 25000 KW

Further compression of 110000 Nm^3/h = 121000 m^3/h (1 atm abs.) from 26.5 to 325 atm abs, in stages 4 to 6 of the 6-stage piston compressors.

Isothermal capacity req'd. for 1 $m^3/min.$ from
1 atm to 26.5 atm abs. = 7.3 PS
Isothermal capacity req'd. for 1 $m^3/min.$ from
1 atm to 325 atm abs. = 12.9 PS
Nis = (121000/60) x (12.9 - 7.3) = 11300 PS
Isothermal efficiency Eis = 0.65
Effective capacity req'd. Ne = 11300/0.65
= 17400 PS
= 12800 KW

Required Capacity of the 6-Stage Compressors

$$\frac{\text{Stages 1 to 3}}{25000\text{ KW}} + \frac{\text{Stages 4 to 6}}{12800\text{ KW}} = \frac{\text{Stages 1 to 6}}{37800\text{ KW}}$$

Compression of 100000 Nm^3/h = 115000 m^3/h (1 atm abs) from 300 to 725 atm abs. in Booster Compressor.

According to experiments by Dr. Pirzer-Lu, suction capacity = 46 m^3/h @ 300 atm abs. and 30°C, pV-deviation 1.2.

Therefore, suction capacity, based on 1 atm abs. and 30°C

V = 46x300/1.2 = 11500 m^3/h each booster compressor.
Isothermal capacity req'd. Nis = 363 KW
" efficiency Eis = 0.80
Effective capacity req'd. Ne = 455 KW

10 operating machines req'd. 4550 KW.

Required capacity of booster compressors = 4550 KW
Total compressor capacity required = 37800 + 4550 = 42350 KW

Electric Losses:

a). 6-stage compressor:
4.5% generator loss
0.5% cable "
3.5% motor loss (synch. mot.)
8.5% total loss.

Turbine capacity:
25000/0.915 = 27400 KW, stages 1-3
12800/0.915 = 14000 KW, stages 4-6
= 41400 KW, stages 1-6

b). Booster compressor:
4.5% generator loss
0.5% cable "
8.0% motor " (synch. mot.)
13.0% total loss.

Turbine capacity:
4550/0.87 = 5200 KW for booster compressors.

For the total required compressor capacity of 42350 KW, 46600 KW must be furnished by the power plant turbine which means an electrical loss of 4250 KW.

In turbo precompression from 1 to 28 atm abs., with the compressor directly connected to the steam turbine, further compression is done in 4-stage piston compressors with synchronous motor drive, because the latter must maintain the COS Ø (power factor) of the entire circuit.

Required capacity of piston compressors = 12800 + 4550 = 17350 KW.
Electrical losses = 8.5%
Therefore, turbine capacity = 17350/0.915 = 19000 KW.

According to the preceding, there still remain for turbo precompression 46600 - 19000 = 27600 KW.

The isothermal capacity, Nis = (190000/60) x 7.4
= 23400 PS
= 17400 KW.

If, because of the final pressure of 28 atm abs, we assume only an isothermal efficiency Eis = 0.59, we obtain the effective capacity required of the turbo compressor and therewith also the turbine capacity

$$Ne = 17400/0.59 = 29500 \text{ KW},$$

i.e. the turbine capacity is thereby increased by

$$29500 - 27600 = 1900 \text{ KW}.$$

With a price for power of RM 0.02/kwh, the cost is, therefore, increased by 8000 x 1900 x 0.02 = RM. 305000/ann. However, since about RM. 4000000 are saved in the cost of plant, which, at only 10% capital burden still amounts to RM. 400000/ann, turbo precompression is economical even in this case. Here, we have not even considered that the lubricating oil consumption is reduced by half of that otherwise required and that the cost of operating personnel and repairs is less than for piston compressors.

Turbo precompression also saves material in the booster piston compressors, if the elimination of the heavy machinery in the low pressure stages is utilized by increasing the RPM of the piston compressors from 125 to 150. This increase in RPM is permissible without question, because the stages requiring great massive strength are no longer used. Neither does this 20% increase in RPM imply any risk for the plant, because the well known 725 atm booster unit compressors have been running satisfactorily for several years @ 147 RPM.

The demand for economy in construction materials must not remain merely a demand, it must be put into practice.

Experiences with Turbo Compressors

Leuna Werke, 29 March 1943

Since the end of 1939 Leuna has had a turbo compressor in operation for compressing catalyst gas from 0 to 29 atm. abs. max. (analysis: 29.1 CO_2, 3.0 CO, 49.5 H_2 and 18.4 N_2/ density 0.81). This machine has been working to our entire satisfaction after overcoming initial operating difficulties.

These satisfactory operating experiences have induced us to propose the installation of a similar compressor, but with increased capacity for our hygas compression.

The turbo compressor delivers about 40000 m^3/h @ 15°C and 755 mm Hg, and at the present time, works together with other piston compressors driven by electric motors or gas engines.

The total quantity of gas required for this department is about 200000 m^3/h. The turbo compressor takes the base load, so that no regulation is normally required. In a sudden failure of the compressor because of operating disturbances or repairs, 4/5 of production can, therefore, be maintained.

Since the catalyst gas hardly varies in composition and density, no difficulties are experienced by displacement of the pumping limit.

From the above description of our operating conditions, it follows that:

1). A turbo compressor for H_2-rich gases should be built for a minimum capacity of 50000 - 60000 m^3/h.

2). The turbo compressor should operate on the base load, where possible, and work together with piston compressors, so that

a). the production is not reduced too much in case of failure, because of its large capacity and

b). the minimum required thruput for CO_2-cleaning or pressure conversion is assured.

3). Turbo compressors can be used only in a new plant, in which the composition and density of the gases is fully known, so that the RPM and number of stages can be definitely determined. In turbo compressors with steam turbine drive, only very limited adjustments can later be made without disturbing operations for variations in gas density within the permissible regulation (shifting the pumping limit, RPM and capacity).

4). The regulating range of a turbo compressor with steam drive depends upon its pumping limit. According to our experience, the pumping limit is 70% of full load in the most favorable case.

As a rule, much less gas is at first required when a new plant is started, so that the capacity can be reduced only by very uneconomical recycling.

When only 3 machines are in operation, fairly large jumps in capacity occur in the course of further plant expansion by an increase in the total capacity.

With turbo compressors alone, operations are difficult to maintain during operating disturbances in case the required quantity drops below the pumping limit of the last machine. In this case we must recycle and at the same time deliver a quantity of gas difficult to regulate.

5). In a sudden failure of a turbo compressor, the reserve compressor can be operated only after about 3 to 4 hours, if the turbine is cold. If the turbine is hot, this time is reduced to 1/2 to 1 hour, i.e. 1/3 of the production drops off for 1 or 3 to 4 hours.

6). The advantage of a turbo compressor, which delivers gas almost free of oil, may have just the opposite effect, if the gas contains H_2S, CO_2 and traces of O_2. In this case, considerable corrosion will take place in the coolers and the pipe line bends behind the coolers at sub-dewpoint conditions because the iron lacks the protective oil coating always present in the piston compressor. In Leuna, e.g. considerable corrosion and erosion took place in the end sections of the coolers and in the pipe line bends between the second stage cooler and the third stage suction nipples, which weakened the walls so much that one of the bends broke apart during operations.

To the items of comparative cost and/or iron requirement between piston and turbo compressors in Mr. Wanser's lecture, we wish to remark that:

1). The extent of repairs and the time required to make them is difficult to determine when a turbo compressor is taken out. Continuous uniform operation can, therefore, not be depended on with just one reserve compressor with 3 in operation. Consequently, 2 reserve compressors should properly be provided.

2). The comparison in the building volume and the costs and iron requirements, must be revised, because the lecturer assumed that power production was simply taken out of the power plant and transferred to the compressor building.

Therefore, the additional differences in figures growing out of this regrouping or subdivision into smaller units and possible greater distance between the boiler or power house must be taken into consideration as follows:

a). possible reduction in the power house building volume,

b). possible increase in the building volume of the return cooler plant with the pump drives,

c). possible increase in the building volume for the pipe lines (difference in distance between power or compressor house from the boiler house for steam supply and gas lines), and

d). increase in the building volume of the condensers (division into smaller units).

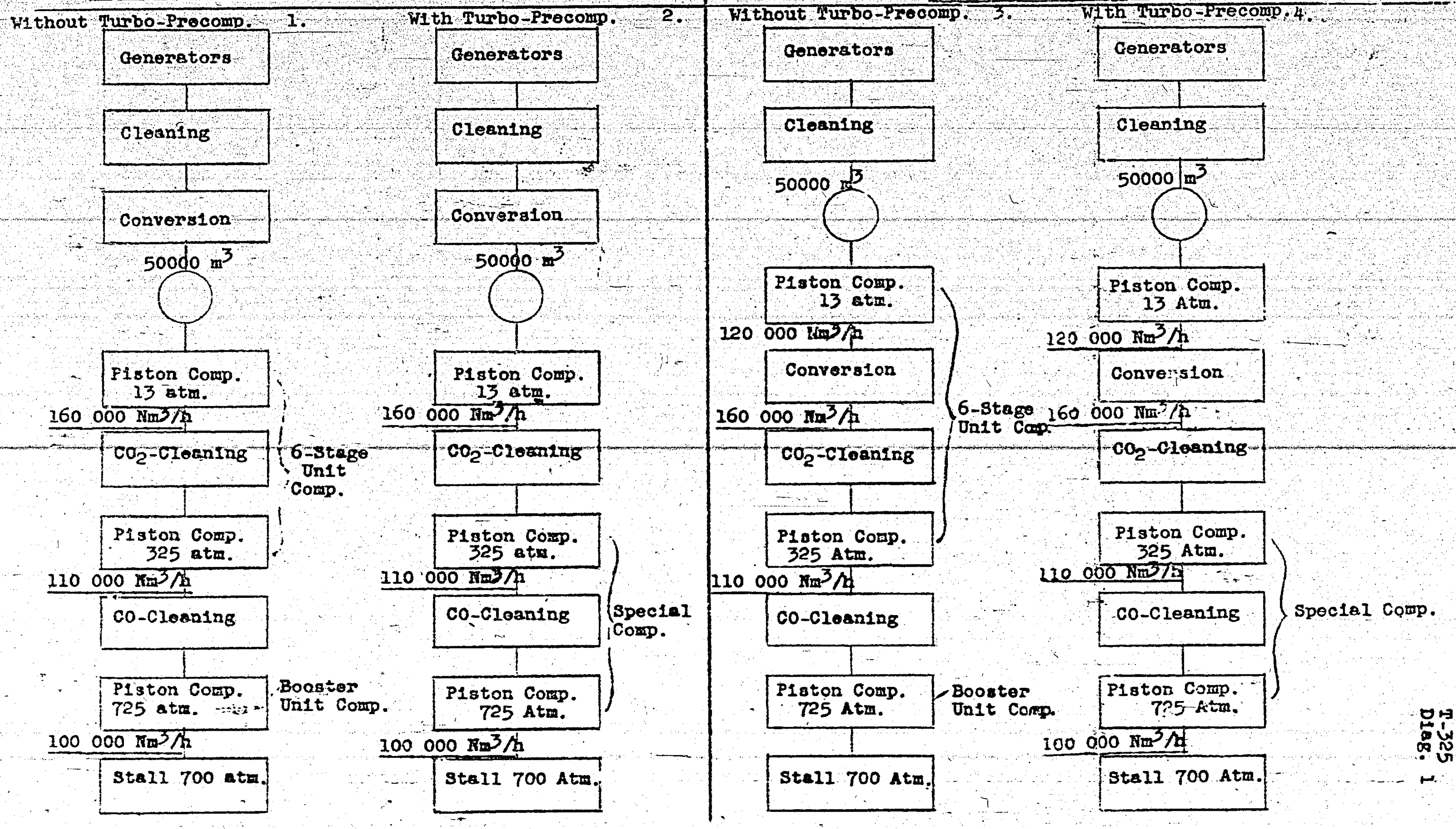
We consider it proper that our opinion should be submitted to MCB and the Reichs-Office for Industrial Expansion, in view of the fact that these points have been definitely cleared up in practice.

/fkp

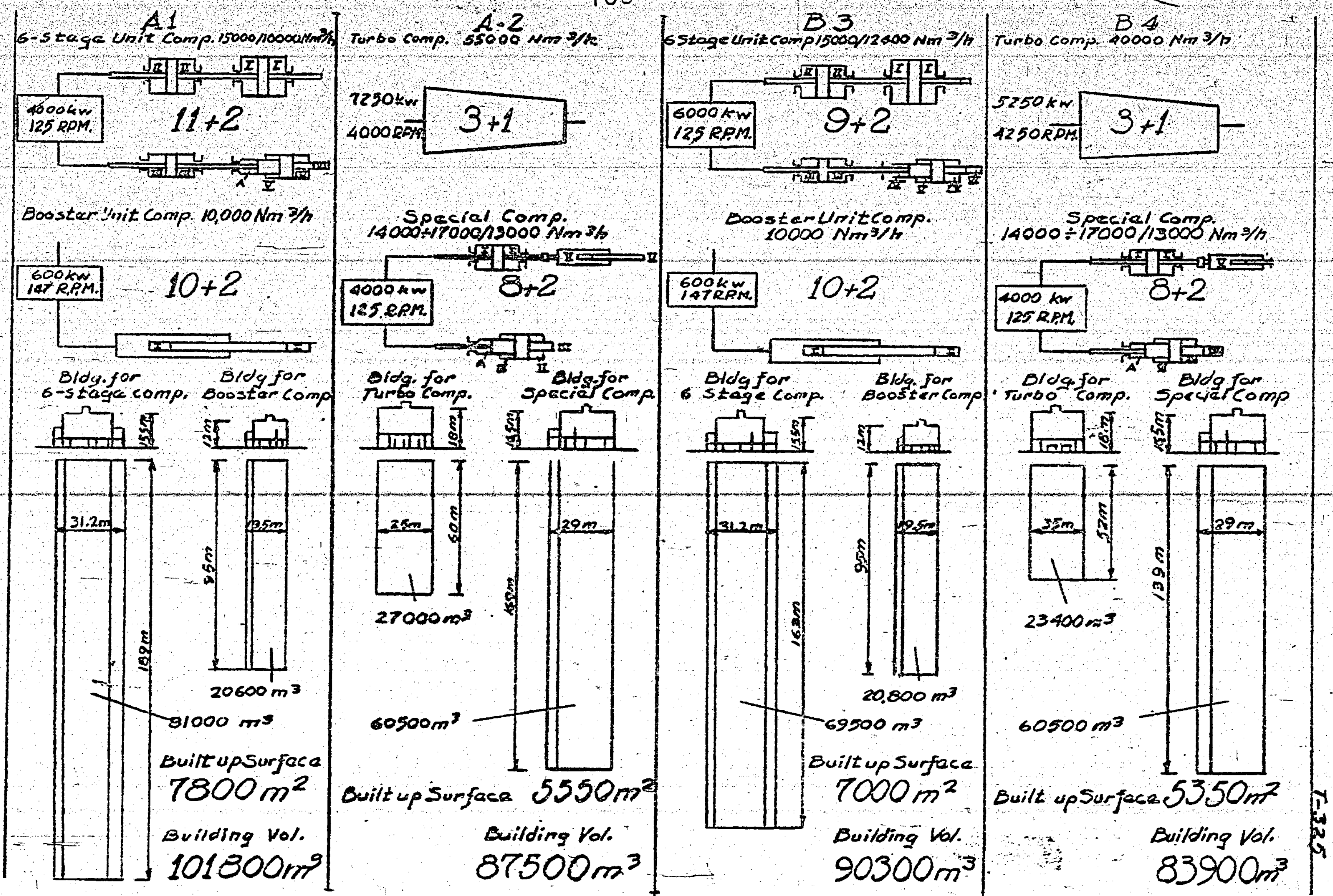
PRESSURE H_2 PRODUCTION

A. Pressureless Conversion

B. Pressure Conversion



T-325
Diag. 1


A1
6-Stage Unit Comp. 15000/10000 Nm³/h
4000 kw
125 RPM.
11+2
A
V
Booster Unit Comp. 10,000 Nm³/h
600 kw
147 R.P.M.
10+2
Bldg. for
6-stage comp.
Bldg for
Booster Comp
15.5m
12m
31.2m
13.5m
95m
189m
20600 m³
81000 m³
Built up Surface
7800 m²
Building Vol.
101800 m³
A-2
Turbo Comp. 55000 Nm³/h
7250 kw
4000 RPM.
3+1
Special Comp.
14000÷17000/13000 Nm³/h
4000 kw
125 RPM.
8+2
A
Bldg. for
Turbo Comp.
Bldg. for
Special Comp.
18m
14.5m
25m
60m
27000 m³
159m
29m
60500 m³
Built up Surface 5550 m²
Building Vol.
87500 m³
B3
6 Stage Unit Comp 15000/12400 Nm³/h
6000 kw
125 R.P.M.
9+2
Booster Unit Comp.
10000 Nm³/h
600 kw
147 R.P.M.
10+2
Bldg for
6 Stage Comp.
Bldg. for
Booster Comp
15.5m
12m
31.2m
95m
19.5m
163m
20,800 m³
69500 m³
Built up Surface
7000 m²
Building Vol.
90300 m³
B4
Turbo Comp. 40000 Nm³/h
5250 kw
4250 RPM.
3+1
Special Comp.
14000÷17000/13000 Nm³/h
4000 kw
125 R.P.M.
8+2
A
Bldg for
Turbo Comp.
Bldg for
Special Comp
18.7m
13.5m
35m
52m
23400 m³
139m
29m
60500 m³
Built up Surface 5350 m²
Building Vol.
83900 m³

Diag. 2.
T-325

POWER DATA: A1	A2	B3	B4
Power Req'd. at the Comp. Shaft. 6-Stage Comp. 36600 kw Booster Comp. 4500 kw 41100 kw	a) Turbo-Comp. 21300 kw b) Spec. Comp. 21800 kw 43100 kw	a) 6-Stage Comp. 31800 kw b) Booster Comp. 4500 kw 36300 kw	a) Turbo-Comp. 15750 kw b) Spec. Comp. 21800 kw 37550 kw
Power Plant Capacity Req'd 45170 kw	Pow. Pl. Capacity 45100 kw	Pow. Pl. Capacity 39950 kw	Pow. Pl. Capacity 39550 kw
Cooling Water/h @ 8°C Temperature Rise: a) 6-Stage Comp. 44x35° 3850 m^3 b) Booster Comp. 40x32 120 m^3 3970 m^3	Cooling Water: a) Turbo-Comp. 2700 m^3 b) Spec. Comp. 2000 m^3 4700 m^3	Cooling Water: a) 6-Stage Comp. 9 x 350 = 3150 m^3 b) Booster Comp. 10 x 12 = 120 m^3 3270 m^3	Cooling Water: a) Turbo-Comp. 3 x 500 = 1500 m^3 b) Spec. Comp. 8 x 250 = 2000 m^3 3500 m^3
Lubricating Oil/24 hrs. a) 6-Stage Comp. 44x10 440 kg b) Booster Comp. 40x15 390 kg 4) 85% of this oil is recovered in oil regeneration 4) 830 kg Loss: 135 kg	Lubricating Oil: a) Turbo-Comp. 18 kg b) Spec. Comp. 400 kg 4) 418 kg Loss: 55 kg	Lub. Oil: a) 6-Stage Comp. 9 x 40 = 360 kg b) Booster Comp. 10 x 45 = 450 kg 1) 810 kg Loss: 122 kg	Lub. Oil: a) Turbo-Comp. 18 kg b) Spec. Comp. 400 kg 1) 418 kg Loss: 65 kg
Machine Personnel a) 6-Stage Comp. 15 men b) Booster Comp. 7 men 22 men	a) Turbo-Comp. 4 men b) Spec. Comp. 11 men 2) 14 men 2) By elim. 1 Turbogenerator 1 mechanic is saved, = 14 men.	a) 6 Stage Comp. 12 men b) Booster Comp. 7 men 19 men	a) Turbo-Comp. 4 men b) Spec. Comp. 11 men 2) 14 men
Finished Machine Weights a) 6-Stage Comp. 13 . 205 = 2665 t b) Motors 13 . 69 = 897 t } 3562 t c) Booster Comp. 12 . 38 = 456 t d) Motors 12 . 21 = 252 t } 708 t 4270 t	a) Turbo-Comp. 4 x 100 = 400 t b) Turbines 4 x 30 = 120 t } 520 t c) Spec. Comp. 10 x 188 = 1880 t d) Motors 10 x 69 = 690 t } 2570 t 3) By elim. 1 Turbogenerator, this val. is red. by 200 t 3) 3090 t	a) 6-Stage Comp. 11 x 218 = 2398 t b) Motors 11 x 69 = 759 t } 3157 t c) Booster Comp. 12 x 38 = 456 t d) Motors 12 x 21 = 252 t } 708 t 3865 t	a) Turbo-Comp. 4 x 90 = 360 t b) Turbines 4 x 25 = 100 t } 460 t c) Spec. Comp. 10 x 188 = 1880 t d) Motors 10 x 69 = 690 t 3) } 2570 t 3030 t
New Machine Costs a) 6-Stage Comp. 13 . 338 000 = 4 394 000 b) Motors 13 . 117 000 = 1 521 000 } RM 5 915 000 c) Booster Comp. 12 . 83 000 = 996 000 d) Motors 12 . 39 000 = 468 000 } RM 1 464 000 RM 7 379 000	a) Turbo-Comp. 4 x 310 000 = 1 240 000 b) Turbines 4 x 140 000 = 560 000 } RM 1 800 000 c) Spec. Comp. 10 x 336 000 = 3 360 000 d) Motors 10 x 117 000 = 1 170 000 } RM 4 530 000 4) By elim. 1 Turbogenerator this val. is red. by RM 720 000 4) RM 5 610 000	a) 6-Stage Comp. 11 x 356 000 = 3 916 000 b) Motors 11 x 117 000 = 1 287 000 } RM 5 203 000 c) Booster Comp. 12 x 83 000 = 996 000 d) Motors 12 x 39 000 = 468 000 } RM 1464 000 RM 6667 000	a) Turbo-Comp. 4 x 270 000 = 1 080 000 b) Turbines 4 x 115 000 = 460 000 } RM 1 540 000 c) Spec. Comp. 10 x 336 000 = 3 360 000 d) Motors 10 x 117 000 = 1 170 000 } RM 4 530 000 4) RM [illegible]
Operating Costs Without Capital Charges & Repairs Current 45 170 kw . 2 Pf = 90 340 Pf Water 3 970 m^3 . 2 Pf = 7 940 Pf Oil Loss 3.6 kg . 150 Pf = 540 Pf Oil Regener. 71.4 kg . 10 Pf = 714 Pf Personnel 22 men . 150 Pf = 3 300 Pf 102 834 Pf RM 1028.34/h	Current 45 100 kw . 2 Pf = 90 200 Pf Water 4 700 m^3 . 2 Pf = 9 400 Pf Oil Loss 2.5 kg . 150 Pf = 375 Pf Oil Regener. 14.8 kg . 10 Pf = 148 Pf Personnel 14 men . 150 Pf = 2 100 Pf 102 223 Pf RM 1022.23/h	Current 39 950 kw . 2 Pf = 79 900 Pf Water 3 270 m^3 . 2 Pf = 6 540 Pf Oil Loss 5.1 kg . 150 Pf = 765 Pf Oil Regener. 28.7 kg . 10 Pf = 287 Pf Personnel 19 men . 150 Pf = 2 850 Pf 90 342 Pf RM 903.42/h	Current 39 550 kw . 2 Pf = 79 100 Pf Water 3 500 m^3 . 2 Pf = 7 000 Pf Oil Loss 2.5 kg . 150 Pf = 375 Pf Oil Regener. 14.8 kg . 10 Pf = 148 Pf Personnel 14 men . 150 Pf = 2 100 Pf 88 723 Pf RM 887.23/h

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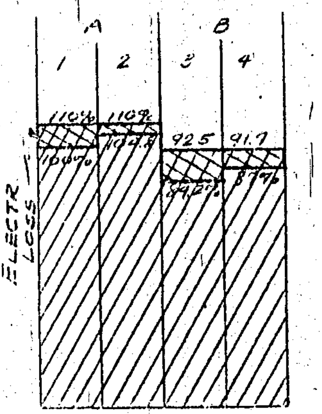
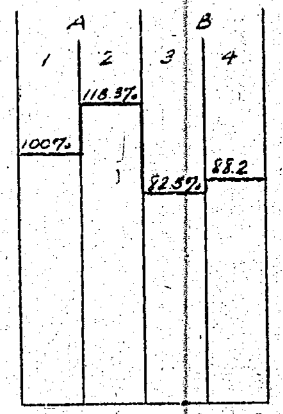
GENERATOR & COMP. CAPACITY



SCALE = 1cm = 5000KW

FIG. 1

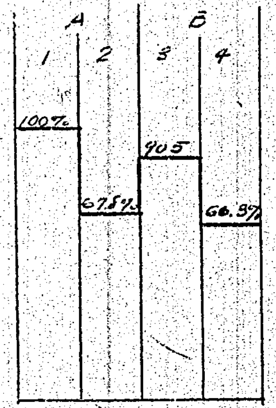
COOLING WATER REQ'D / HOUR.



SCALE 1cm = 500m³

FIG. 2

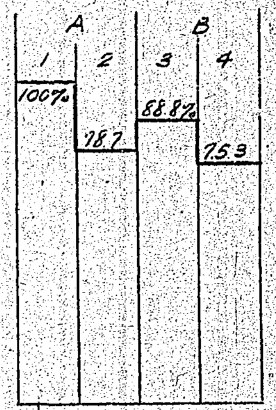
NET MACHINE WEIGHTS



SCALE 1cm = 500T

FIG. 5

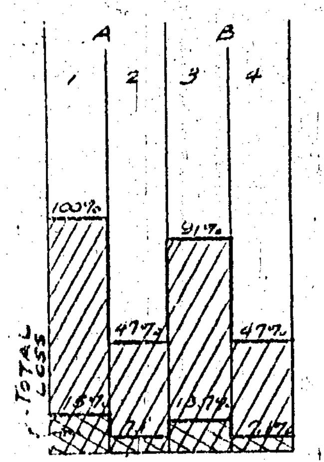
BUILDING VOLUMNS



SCALE 1cm = 10000 m³

FIG. 6

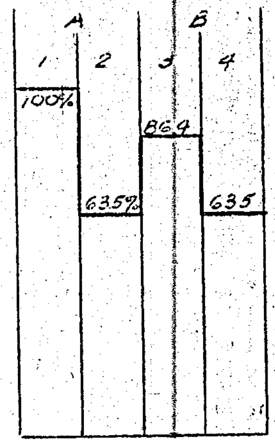
LUB. OIL REQUIRED AND LOSS / HOUR



SCALE 1cm = 5 kg.

FIG. 3

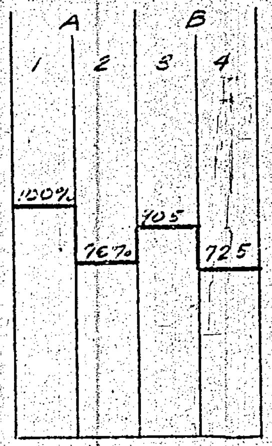
MACHINE PERSONNEL PER HOUR



SCALE 1cm = 2 MEN

FIG. 4

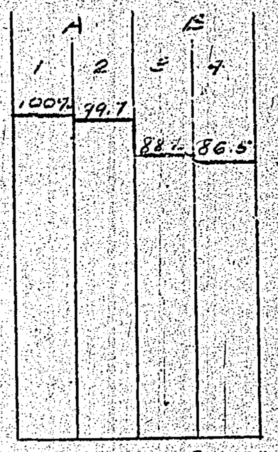
NET MACHINE COSTS



SCALE 1cm = RM 1000 000

FIG. 7

OPERATING COSTS / HR. WITHOUT CAPITAL BURDEN AND REPAIRS



SCALE 1cm = RM 100

FIG. 8

C.H. Equipment

T-326

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

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KCEraun
4-17-47

Bellows Lenses (Sealing Ring Gaskets)

(A Roundtable Discussion of their Properties)

(See also T-245)

By Ch. Eng. Berger (I.G.Lu)
Blechhammer, 11 May 1944

Since the coal stalls at Blechhammer are now operating satisfactorily with bellows lenses, the present state of the matter of bellows lenses can be summarized to a certain extent. To the repeatedly expressed opinions, we take the following position. Under discussion were the two (2) sizes NW 110 and 135 mm.

1): Strain on Bolts

NW 135 is stressed 10% more than NW 110 and NW 100. This was taken into consideration in determining the bolt material, by specifying 10% greater strength for the 1-3/4" rods used for bolts. However, the lens material still has to withstand correspondingly greater stresses.

2). Stiffness of Bellows Lenses, Compared to Solid Lenses.

The solid lenses are undoubtedly stiffer than the bellows lenses and contain no factor of doubt with respect to their manufacture in their outer form of construction. (No difficulty in manufacture). It has, however, not been definitely determined whether the solid lenses are unnecessarily oversized.

3). Accuracy in the Making of Bellows Lenses.

A number of average lenses, particularly the NW 110, showed a crack (regular and irregular), the cause of which could not be determined.

4).

One form of leak caused by too rigid mounting of the hairpin coils in the preheater has already been eliminated. The expansion and contraction in the connecting lines in the preheater and in the risers has also been improved.

5). Cause of Leaks

How much the above mentioned points, individually or collectively, have contributed to leaks can be determined only by prolonged observation in the plant and in the testing station.

/phl

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

GELSENBERG BENZIN A.-G.

To I.G. Farbenindustrie A. G.
High Pressure Experiments
Ludwigshafen am Rhein

Gelsenkirchen,
6-9-44.

INTERCRYSTALLINE CORROSION IN PIPE LINES.

We have observed since the start of operations in our works that leaks were produced in the different pipe lines after ½ - 1 year operation; these leaks were caused by cracks extending through the whole thickness of the tube wall. Exhaustive investigation has shown, that we were dealing here with intercrystalline corrosion. This damage occurred preferentially in the proximity of welds and on the outside of the elbows. The i.d. of the damaged tubes made of the ordinary steel (St. 35.29) was mostly 150 mm. The attacks are chiefly observed near the coal catchpot, but also in the pipe lines carrying the B middle oil. We may state on the strength of exhaustive investigations, that the phenol content of the oil was the cause of the attacks.

The occurence of such corrosion is the result of combined action of three factors, namely:

1) the use of material apt to be corroded;

2) strains in the material;

3) chemical attack by the feed.

The presence of the feed can not be avoided; we may therefore look for help in changing the first two factors. One must consider therefore the use of non-corroding material, such as alloy steels or a corrosion resistant IZL steel. Alloy steel is at present entirely excluded, and the procurement even of the IZL is at present so difficult that we may not count on its introduction. (It must be born in mind, that flanges must be made of the same material as the tube themselves, if a far-reaching protection against intercrystalline corrosion is looked for, and the purchase of flanges is particularly difficult.) There remains the possibility of coating the pipes on the inside with a protective coating, e.g. with an enamel or with a baked on artificial resin lacquer. We have already begun experiments with an artificial resin lacquer (Munkalit, from Munk and Schmitz, Cologne). The coating is however dissolved by oil in a short time. Chromplating the insides of the tubes would probably help, but this proceedure appears to be impossible today for tubes of such dimensions. The second factor, the elimination, or at least the reduction of strains, may be achieved by heating the tubes to 600° after welding or bending. The tubes then will merely have to stand the strain from the pressure of the feed, which amounts in our case to 1.5 - 2 kg/mm^2. We carefully anneal the tubes, but with limited success, because the life of the annealed tubes is only slightly longer, than of the unannealed tubes.

The above mentioned damage has become so important of late, that of the five pipe lines available, at least one is out of use because of intercrystalline corrosion, and is being put back in operation. The labor requirements under the existing conditions must be consider intolerable, and we are trying urgently to find means of overcoming this difficulty. We request you therefore to inform us of any experience you may have had in this problem, and which we might successfully use.

GELSENBERG BENZIN Aktiengessellschaft

2 signatures.

Copies to: I.G.Farbenindustrue A.G., Ludwigshafen Rhein
Ammoniakwerk Merseburg - G.m.b.H., Leuna Works
Hydrierwerk Scholven A.G., Gels enk.-Buer
Union Rheinische Braunkohle A.G., Wesseling
Hydrierwerke Pölitz G., Stettin-Pölitz.

W. M. Sternberg

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10/17/46

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

DIRECTIONS FOR OPERATING
HIGH PRESSURE HYDROGENATION EQUIPMENT

No collection of standard operating procedures is available. We have collected below recommendations made from our experience and knowledge; in part they were obtained from the operations of our semi-industrial installations in Ludwigshafen, and in part from the large industrial units, and are arranged as follows:

1) Purging and pressure testing of a high pressure stall
2) Filling a hydrogenation stall with hydrogen
3) Starting a circulation pump
4) Stopping a circulation pump
5) Starting a gas fired preheater
6) Operating a liquid phase stall (coal)
    a) starting
    b) precautions and observations during operation
    c) precautions in case of trouble in a stall
    d) stopping a coal stall
7) Operating a liquid phase stall (tar, pitch, oil)
    a) starting
    b) precautions and observations during the operation of the liquid phase stall
    c) precautions in case of trouble in a liquid phase stall
    d) shutting down a liquid phase stall
8) Operation of a vapor phase stall (prehydrogenation and benzination)

   a) starting a prehydrogenation stall
   b) starting a benzination stall
   c) precautions and observations in the operation of a vapor phase stall
   d) precautions in case of trouble in the liquid phase stall
   e) shutting down a vapor phase stall

9) Gas circulation and gas scrubbing in the liquid phase

10) Operation and inspection of pumps and compressors.

1) FLUSHING AND PRESSURE TESTING OF A HYDROGENATION STALL.

Nitrogen is passed through the whole equipment until analysis of the gas taken behind the cooler indicates less than 4% oxygen (preferably about 1%). The whole stall is then filled to a pressure of 300 or 700 atm. through the usual gas and feed lines. When the intended pressure is reached, the whole installation remains under that pressure for at least 4 hours to observe any drops in pressure. The pressure may not drop more than 2 atm per hour. During that time the gaskets, cover, stuffing boxes, etc., are tested by listening and brushing with a soap solution. When the pressure testing is completed, the pressure is released in the whole installation through all the pipe lines, with the stall inlet valve open.

2) FILLING A HYDROGENATION STALL WITH HYDROGEN.

The stall, after being flushed with nitrogen and the pressure released is filled with hydrogen from the pressure side; While doing this, the production of greater pressure differences is avoided. (Testing of manometers, or opening of the stall by-pass). When filling a stall with new catalyst, the length of time to be used in filling given in 8a) must be observed.

3) STARTING A CIRCULATION PUMP.

The shut-off valves on the suction and pressure sides are kept closed, the blind flanges in the intake and outlet of the stalls are removed and the by-pass valve of the pump is opened. The machine is next set under 10 - 20 atmospheres of nitrogen, permitted to run for about 5 minutes, and the pressure released. The process is repeated, and tests are made for oxygen. When the latter drops to below 4 or 1%, filling with hydrogen begins from the suction side of the circulation circuit until the pressure has become equalized. The by-pass valve of the pump is then slowly throttled down.

Should the pressure difference be more than 5 - 10 atm than the difference in the gas circuit, the shut-off valves to the circuit are opened on the pressure side, and the by-pass valve of the pump is simultaneously closed. The man at the circulation difference manometer is to be notified before placing a new gas circulation pump into circuit.

4) SHUTTING OFF A CIRCULATION PUMP.

The machine is stopped by shutting off the drive. The suction and the pressure valves are closed, the by-pass valve of the pump is fully opened and the pressure released into the open. If the circulation pump is to be opened for repairs, it is purged with nitrogen, exactly as during the starting. After a test shows 1 - 1.5% hydrogen, the blind flanges on the pressure and the suction sides are inserted in the gas circuit, and repairs begun.

5) STARTING A GAS PREHEATER.

The preheater is first purged with air in the following way: the circulation blower is started with closed suction and pressure valves, and the suction valve slightly opened. The pressure valve on the blower remains closed at first. The air is sucked in through the pilot burner and blown for half an hour outside by opening the pressure valve of the blower (the pressure valve o on the main burner must remain closed). Tests are made for air (20% oxygen) in the pipe line to the waste burner. In the meantime the blind disc in the fuel gas line to the pilot burner is opened. For the pilot burner a different gas was used than for the main burner.

The pilot burner (safety flame) is lit with a lighter. The blind flange in the fuel gas line to the main burner is only drawn after all the pilot burners burn perfectly. After this is done, fuel gas is slowly fed into the main burner, until the gas ignites (watch the flame; color). When it burns properly, circulation gas is fed into the burner. When opening the valve of the circulation gas to the burner, the flame must be watched, to see it is not extinguished.

When everything is in order in the preheater, the supply of the fuel gas and circulation gas are increased to meet the requirements. The burners are so set, that the oxygen content on the pressure side of the circulation gas be 2 - 3% (testing for CO_2, CO and O_2 in recorder and several daily analyses).

Should some hairpin in a preheater spring a leak (manifested by a sudden rise of the hairpin temperature or by a plume of smoke in the flue on the outside) the stall is rapidly cooled. When the leak is large the fuel and pilot burners are extinguished, the circulation gas blower turned off, the preheater closed off by closing all the valves, and placed under CO_2 or N_2; The stall is immediately put through an emergency let-down. When the pilot gas burner becomes extinguished, their regulating slides are closed and the burners in operation (fuel gas burners) are carefully watched. Should the fuel gas fail, all its regulation valves are immediately closed. The bearings of circulation gas blowers, and, if available, those of the air blowers are all observed hourly. The safety valves in the fuel gas are tested twice a week and the explosion discs on the preheater once a week. The burners are cleaned after 6 - 8 weeks operation, and during shutdown.

6) OPERATION OF A COAL STALL (e.g. of a 4 converter stall with 36 m³ volume)

a) Starting.

After the desired pressure has been reached in the suction side of the stall, the electric valve on the suction side is opened and within 20 minutes, 28,000 m³/h of gas is passed through the heat exchangers and 2,000 m³/h of paste gas to the preheater. A little bubbling gas is passed through all the cold gas lines. The preheater is now heated to temperature, to 220°C at the rate of 30 -35°/h, to 350°C at 15 - 25°/h, and to 415° at 8 - 12°/h. At 170 - 180° in converter I the oil flushing in the circuit (light oil bottoms) is started, 3 m³/h in the heat exchangers and 2 m³/h in the thick paste pass of the preheater. At 290° in converter IV, feed is changed over to pasting oil, and the amounts through the heat exchangers and preheater increased to 10 and 5 m³/h respectively. The correct behavior of the cold gas is tested at 300 - 320°C converter temperature, beginning with the last converter. When the converter temperature reaches 415°, the change over to coal paste is made. The paste load and the reduction in pasting oil are regulated by the temperature rise in the converter (reaction beginning in the stall). The maximum temperature and thruput are usually reached in three hours, and namely: 481° in converters I and II, 480° in converter III, 476 - 478° in converter IV, and 445 - 450° in the hot catchpot. When the oil flushing mentioned above is begun, 200 - 300 liters flushing oil (light oil bottoms) are fed each hour into the desanding, and 2000 - 3000 m³/h of stirring gas into the bottom of the catchpot when the proper liquid level in the catchpot has been reached. Desanding and HOLD-release are put in operation when the hot catchpot is filled to its proper level. The temperature in the hot catchpot is regulated by the amount of solids in HOLD (20 - 25%). The ratio of HOLD: light oil was at about 40:60%. When production is started, 800-1000 li/h of flushing water (condensate) are injected infront of the coldest heat exchanger, 400 li/h in front of the cooler and 300 li/h in the suction side of the circulation gas. The temperature of HOLD is kept at 200 - 220° in front of the let-down, and the cold catchpot at 65 - 70°. With a full stall load the cold gas distribution was: about 20 - 22 m^3/h with the thin paste in the heat exchanger, 15 - 17 m^3 to the thick paste in the preheater, 5000 - 6000 m^3/h to converter I, 10,000 - 12,000 m^3/h to converter II, 8,000 m^3 to converter III, and 5000 - 6000 m^3/h to converter IV. The stall must be operated on such a pressure difference, that the stall pressure (prepressure for cold gas) be not below 15 atm, but the whole stall difference should not exceed 42 atm, with regard to the heat exchangers. All the let-down and emergency let-down pipe lines, as well as the group of let-down orifices are filled with oil while the pressure in the stall is still below the operating pressure. The pressure release steps in the 700 atm stall in front of the valves are 450-500 atm behind them, 200-250 atm directly in front of the conical vessels and 1.5-2 atm inside of them. After the change over to coal, when the amount of solids in the HOLD has reached 15%, it is sent to be worked up; while operating with HOLD (with below 15% solids) it is used as pasting oil.

b) Precautions and tests during the operation of a coal stall.

Emergency let-down pipe line, reserve let-down lines, reserve group of valves for let-down, as well as the de-sanding, are rinsed twice per shift with flushing oul. Safety valves of the 50 atm collector vessel for the let-down are flushed daily with steam condensate, the 2 atm catchpot twice a week with steam, (prevention of formation of ammonium carbonate). All the orifice flowmeters are to be tested by blowing, etc. each shift. The pipe lines to the level indicators in the hot catchpot are daily flushed with gas, and weekly with oil. The let-down orifices of the hot catchpot, also of the caviar desanding, the nozzles in the conical vessels and the emergency let-down towers are inspected once a week. The emergency let-down lines and the throttling orifices in them are tested for erosion after each emergency let-down. The electric valves (rapid shut-off valves) are tested daily in the morning shift. The bearings of the recycle gas and make-up air blowers are under continuous observation. The stall is observed for leaks three times per shift. Check the thermostat temperatures because of the possibility of false temperature indications.

c) Precautions in case of trouble in a stall.

1) runaway converter temperature

Essentially, when the converter temperature runs away, operations are turned over to pasting oil at 490 - 493°C, the amount of fuel gas in the preheater reduced to one half, and if the temperature decreases, care is taken that the temperature does not fall below 415 - 425°C. Should the temperature run away further, efforts are made to reduce the converter temperature by the addition of cold gas or, if available, cold oil in the localities of high temperature. Should the converter temperature reach 510°, one must immediately proceed with the emergency let-down, i.e. the contents of all the converters and the hot catchpot are pressure released simultaneously through the emergency let-down pipe lines through the pressure release tower.

2) Emergency let-down.

Emergency let-down must also be used in the following cases:

Plugging up of the make-up gas (resulting from coking of the converters).

Stoppage in the cold and operating gas supply (causing inability to control the temperature and coking).

Stoppage of paste pumps.

Stoppage of electrical current.

Stoppage of cooling water.

Large leaks in preheater or stalls.

Complete plugging up of converter or lines.

3) Pluggingup.

Incipient plugging up becomes manifest in the increased total pressure difference in the stall. Tests (determination of partial differential pressures) indicate the danger spot (heat exchangers, cooler, pipe lines behind the catchpot), and an increased amount of water injected in front of them, (ammonium salts). As a rule, this will eliminate the plugging up.

4) Heat exchanger short circuit.

A heat exchanger short circuit is made evident by the darkening of the catchpot product and a reduction in the stall pressure difference, as well as by the presence of solids in the catchpot; the stall is cooled and tested, with an eventual replacement of the leaky heat exchanger.

d) Shutting down a coal stall.

The amount of the fuel-gas is cut down to one half, and operations changed over to pasting oil at 475°C. The temperature is kept for sometime at 440°, and the amount of oil reduced in the course of an hour to 10 m^3/h in the heat exchangers and to 5 m^3/h in the preheater. At the converter temperature of 305°, operations are changed over to light oil bottoms, and thruput reduced in one hour to 3 m^3/h in the heat exchanger, and 3 m^3/h in the preheater. The temperature is dropped to 350° C in the converter by 10-15°C/h to 250°C by 15-20°C, and by 20-25°C to 185°C. Injection is then stopped, the gas is cut off in 20-30 minute, and the fuel gas and pilot lights extinguished and blinded. The blower remains in operation until 80-90° hairpin temperature is reached (chrome-nickel thermocouple). The stall is separated from the circuit and the converter and the hot catchpot are pressure released through the valves in the pressure release tower. Each unit is twice to be emptied. The heat exchangers, starting with heat exchanger I are emptied at 150-200 atm. pressure. At about 30-50 atm. hydrogen is blown in a vigorous stream two to three times through the gas intake to the heat exchangers and the paste gas lines to obtain the preheater hairpins free from oil and coal paste. The residual pressure of around 30-50 atm. is released with a closed by-pass through the stall to the outside. The stall is next flushed with nitrogen to below 4% hydrogen, and the blind flanges are inserted.

5) Operation of Liquid Phase Stall.

(e.g. a bituminous coal tar or pitch stall as a four-converter stall with 36 m^3 volume, mineral oil stall with 3 converters, of 27 m^3 volume).

a) Starting.

Heating up: to 220° at the rate of 30-35°/h, to 350° at 15 to 20°C/h, to 450° at 14-17°/h, and to the temperature desired for the throughput at 8°/h. In the coal tar or pitch stalls the amount of operating gas through the heat exchangers is 25,000 to 28,000 m^3/h, and 2,000 for the return of the HOLD, in the petroleum stalls 18,000-20,000 m^3/h over the heat exchangers and 2,000 m^3 in the return of the HOLD. The converter I and the hot catchpot are begun to be filled with the cold HOLD return at 185-220° C (when first starting, a paste with about 20% catalyst is used and added to some suitable heavy oil, such as light oil bottoms) and with make-up feed. At the start, 2 m^3/h make-up feed over the heat exchangers, 1 m^3 make-up feed and 2 m^3/h let-down return (or make-up catalyst, v.s.) directly to the preheater. The thruput is increased as the temperature is raised to 4 m^3/h make-up feed through the heat exchangers and 6 m^3 let-down return, and 1 m^3/h make-up feed to the preheater (in the course of 4-5 hours). After the level has been reached in the hot catchpot, the hot circuit (internal circulation of the catalyst) is begun with 1 m^3/h, and raised in two hours to 10 m^3/h. When filling with make-up catalyst, the changing over to let-down is made as soon as a supply of let-down has become available. At a converter temperature of 475°, up to 1.5% make-up catalyst (referred to make-up feed) is continuously added to the let-down return. The throughput of the make-up feed is increased depending on the let-down concentration and production of let-down. The amount of let-down is kept at 5 - 6 m^3/h. The concentration of the let-down to the desired concentration must proceed slowly over a period of 20-24 hours (especially after a previous filling with fresh make-up catalyst). In the tar and pitch stalls the concentrations of the solids is kept between 25 and 30%, with mineral oil stalls at 20-25%. 3000-5000 m^3/h of stirring gas are introduced into the hot catchpot from below after the temperature had reached 440° C. The concentration of solids in the let-down is regulated in the not fully loaded stalls by regulating the temperature, and after the maximum temperature and full load have been reached, by regulating the injection. As soon as the required concentration of solids has been reached, enough let-down is sent over for working-up as is necessary to maintain a given concentration of solids. The maximum converter temperature in tar stalls was 483°C in converter I and II, 478-480° in converter III and 474-478°C in converter IV, with 442-450° in the hot catchpot; the HOLD temperature was 150-160°, in the catchpot 65-70°. The maximum converter I and II temperature of the mineral oil stalls was 484-486°C, converter III 481°, converter IV 478-480°, 435-442° in the hot catchpot, 150-160° in the let-down and of the cold catchpot 65-70°. The catalyst paste of the tar and pitch stalls was made with light oil bottoms produced (20%), in petroleum stalls with the HOLD (10%).

b) Precautions and Tests during the Operations of the Liquid Phase Stall.

The cold gas is added slowly (in stages), to prevent the converter contents from being entrained into the hot catchpot, filling it, and having the solids reach the cold catchpot to foam and be carried into the circuit which will result in increasing the pressure differences in the circuit. The solids content in the let-down should not materially exceed a maximum, lest local reactions be produced. In tar and mineral oil stalls the running away of a converter unit is not so dangerous, because reactions there always remain localized. Emergency let-down as a rule is not required, a temporary lowering of temperature is usually sufficient. Tests and supervisions are otherwise no differant from the coal stall.

c) Precautions in case of trouble in the Liquid Phase Stall.

In case of a total interruption of power or other catastrophies, the stalls are only shut down on the suction side of the circuit, to utilize the total gas volume of the circuit, the circuit vessels, the circuit gas scrubbing, etc. for the emptying of the preheater hairpins and the heat exchangers. The gas intake and the paste gas regulating valves remain open, all the cold gas valves are closed. All the electrically operated valves (rapid closure valves) are immediately opened in the following order: converter I, converter II, converter III, converter IV, hot catchpot angle valve, and finally the valve at the emergency let-down. (When there are coal stalls in addition to tar or mineral oil stalls, the coal stall is handled first, because the danger of coke formation in the hairpins is here the greatest; in tar or mineral oil stalls there are at leat 5-7 minutes time available for emergency let-down). The pilot burners and fuel gas in the preheaters is turned off, all electric drives of the machines, etc., are turned off. As soon as possible after the emergency let-down all the pipe lines of the let-down, emergency let-down and the de-sander, as well as the groups of orifices, are put under flushing oil (to prevent any plugging up). One gas return blower from each preheater is set to the outside for further cooling of the preheater. As soon as possible efforts must be made to put the stall back under pressure and flush it with gas passing at 30-50 atm.

When the hot circuit is stopped, the cold return of the let-down is increased from 6 to 10 m^3/h to prevent to production of local reactions, and therefore coking which might result from slowing down of the motion; the temperature also must eventually be lowered.

The running away of the temperature is far less dangerous than in the coal stall. Should it however be impossible to master the temperature (persistent high temperature), then the same procedure must naturally be followed as in a coal stall.

Leaks, short circuit in heat exchangers and plugging up are handled as in coal stalls.

d) Shut Down a Liquid Phase Stall.

The supply of fresh catalyst is immediately stopped, the temperature lowered at the rate of 8-12°/h, with a corresponding curtailment of the make-up feed, at 440° C the return of the letdown is reduced in the course of 2 - 3 hours to 2 m^3/h, and the required amount of fresh feed is reduced enough to produce 5-6 m^3/h of let down. At 350° C converter I is changed over to its own light oil bottoms (about 4 m^3/h over the heat exchangers and 2 m^3 to the preheater). When less than 15% solids are produced in the let down it is sent to the injection feed. When the converter I temperature reaches 185°, the preheater is extinguished, injection, gas thruput, hot circuit are stopped, the stall disconnected from the circuit and expanded through the nipple in the emergency expansion tower (exactly as in coal stalls) finally flushed with nitrogen and the shut-off flanges inserted.

8. Operation of a Vapor Phase Stall at 300 atm.

a. Starting up of a prehydrogenation stall (catalysts 5058 and 8376, (e.g. a 3 converter stall of 27 m^3 volume).

In stalls with fresh catalyst, particularly 5058, the following schedule of filling must be adhered to protect the catalyst (rapid heating up and bursting of the catalyst pills): one hour to 10 atm, one hour from 10-30 atm, one hour from 30 - 100, one hour from 100 - 300. The temperature in the converters must be watched: it should not exceed 150° C. When filled, 40,000 m^3/h of gas is set to pass after 20 minutes, and the further heating up to 250o C is done at the rate 15° C/h, to 350° at 10°/h.

The cold gases, starting at the back, must be tested when the converter temperature reaches 300° C. The injection is begun when converter I has a temperature of 355° C. The original injection of 4 m^3/h is increased hourly by 1 m^3/h up to 20 m^3/h, and then by 1/2 m^3/h until the full load is reached. After the thruput has been reached the gas supply is reduced by 1000 m^3/h to 30,000 - 35,000 m^3/h (depending on the stall operation). The temperature is set depending on the phenol and nitrogen values of the hydrogenated product. The partial pressure of hydrogen should not drop to below 235 atm. With freshly filled catalyst and good heat exchange, stall operate authothermally for a long time. 1000 - 1500 li/h of flushing water (condensate) in front of heat exchanger II is used. In combination stalls with catalyst 5058 and 8375 the 5058 catalyst occupies the last position.

When filled with new catalyst, the dust is blown out before the stall is closed by alternately forcing nitrogen through it from above and from below.

b) Starting a Benzination Stall (Catalyst 6434) (e.g. 4 converter stall, 36 m^3)

The filling, starting and heating up as in the prehydrogenation. Injection is begun at 355° C (6 m^3/h) and increased by 2 - 4 m^3/h until the required load is reached (maximum load of a 4 converter stall is 45 - 50 m^3/h). The flushing water to heat exchanger 2 is added only as required. All contact with the injection feed of the prehydrogenation is prevented on the feed side (poisoning of the catalyst). A separate gas circuit is required for benzination, if no recycle gas scrubbing in the water has been provided.

The amount of operating gas was 25,000 - 30,000 m^3/h, with the hydrogen partial pressure not dropping below 235 atm.

c) Precautions and Tests to be Used During the Operation of the Vapor Phase.

The formation of a liquid phase which would form below 355° must at all times be avoided. Should the temperature become less than 355°, injection must be immediately stopped, because when the vapor phase reappears, the reaction will become uncontrollable, and will be carried over into the connecting pipe line, which may spring a leak or burst. The catalyst pills will crumble even if a runaway can be avoided. When the temperature difference inside the stall rises, the place of plugging has to be located. If the plugging is in the heat exchanger return pass, a double amount of flushing water is to be used for a short time, but suddenly. Care must be taken of the prepressure (not under 10 atm.) when the pressure difference becomes high, and the injection as well as the amount of gas going through are proportionately reduced.

d). Precautions to be Taken in Case of Trouble in the Vapor Phase.

In case of a short circuit in the heat exchanger, which becomes apparent by a darkening of the catchpot product, the injection is turned off, and the stall is operated dry and cold. The stall is shut down, the pressure released and the heat exchangers tested.

When the current is off, injection is immediately stopped. If the power is only off for a short time, operations may be resumed with an intake temperature of 355° C.

When the hydrogen supply is off, as well as in case of larger amounts of CO, the injection and the make-up gas are discontinued and the gas recycle continued, until the difficulty is corrected. When the trouble is over, the stall is brought back to intake temperature, and the operations resumed.

Smaller amounts of CO (up to about 1-2% depending on duration) can be overcome by injection of cold gas.

Leaks and plugging up are handled as in the coal stalls.

If a stall is shut down and the pressure released because of too strong reaction, the pressure is released slowly, watching the thermocouples in the connections. Too rapid pressure release may cause local reaction rates to be carried further and the connecting pipe lines may burst (must be judged from conditions).

e). Shutting Down the Vapor Phase.

The injection is reduced by 2 - 4 m^3/h, and the temperature accordingly (9 - 14°/h). The injection is completely stopped when the load is about 4-6 m^3/h at 355° C, equally the water injection. While the injection is being reduced, the amount of operating gas is increased in 4 hours to 40,000 m^3/h. At 350° the converters are operated dry for about 4 hours. The converters are cooled to 250° C at 14 - 17°/h and to 115° at 18 - 22°/h.

9. Gas Circulation and Gas Scrubbing in the Liquid Phase.

The suction side of the liquid phase gas circuit is steam heated and is insulated (formation of propane hydrate at low temperatures). On the pressure side the temperature is abt. 55-60°, on the suction side 60-65°. The circulation gas is cooled to 30 - 35° in the circulation gas cooler (not below 30°, because of danger of propane hydrate formation), and the condensate injected on the suction side, as well as any entrainment from the catchpot, are continuously drawn off from the catchpots. The gas is uniformly distributed into the scrubbers in operation. The maximum load of a scrubber (15 m^3 volume) was 75,000 m^3/h of gas and 45 m^3/h oil. The scrubbing oil was returned to the scrubber through 2 pressure release machines, 2 supply circulation pumps and 2 additional pumps. The oil scrubber temperature was between 35 and 40°. The condition of the scrubbing oil was determined by measuring the time of breaking of the foam; with over 60 sec. for the breaking down of the foam after 3 - 5 minutes shaking in the reagent bottle, the scrubbing oil is used up and is replaced. The fractional pressure release of the wash oil proceeds from 700 atm. to 38 atm, and then further to 1 atm. The pressure drop in the circuit was currently supervised by recording, and so was the temperature. Observation for leaks in the circuit were made twice a shift. The catchpot vessels on the pressure side were stripped twice a shift and the vessels on the suction side of the circulation pump were stripped until gas came whenever the warning signal was sounded (level indicators with alarm signals). the electrical valves and the Ferranti slides in the circuit were continuously watched and serviced (greasing, etc.). Circuits which have been out of use, and cooled circuits, are tested with 40,000 - 50,000 m^3/h gas, and heated up in about 4 - 5 hours. The liquid level gauges are tested once a shift. The circulation gas difference was kept at a 50 atm. max. in the liquid phase and in the vapor phase at 40 atm. The amount of reserve circulation gas (determined by the circulation gas differential reading) was at least equal to the capacity of a gas circulation pump (70,000 - 80,000 m^3/h).

10. Handling the Machines.

All machines not in operation were briefly started once in shift (to prevent corrosion from standing). Paste presses which had been in operation were flushed for half an hour at a low rpm first with pasting oil, then with light oil bottoms. The injection pumps for middle oil sulfurized with H_2S were flushed with unsulfurized feed before shutting them down (prevention of corrosion). All machines sent over for repairs must have their power drive connections blocked.

W. M. Sternberg.

DR. STORCH

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

KCBraun
4-21-47

Filtration of Letdown from Stall 804 at 700 Atm & 25 MV with Middle Oil Pasting.

Comparison with Column Filter

(See also T-177, T-206,
T-271 & T-301.)

By Pfinmann, I.G.
Ludwigshafen, 23 July 1942

The results of experiments in the filtration of letdown from Stall 804 at 300 atm and 23.5 MV, with a thruput/space/time of 0.5 Upper Silesian coals were compiled in a report of February 23, 1942, including:

a) - a column filter, 0.2 m^2 (Kerzenfilter)
b) - a special Dorr filter for thin layer filtration
c) - a suction filter rebuilt by us for thin layer filtration.

The results of filtration from the three (3) types of filters were entirely satisfactory as to removal of ash; the bitumen obtained contained 0.1% ash and mostly less. The filter yields from a column filter with letdown, which in a test in the test pressure filter had required 1-3 minutes, was about 300-400 kg/m^2/h net filter time, which, however, was reduced to about 120-200 kg by the operations of opening, cake removal, etc. With the Dorr filter the yield, using Kieselgur as filter layer, was 150-200 kg/m^2/h; with quick removal, i.e. more than 1% Kieselgur consumption, even 200-300 kg. Almost the same result was obtained with the rebuilt cell filter. But since it only requires about 2 hours to apply a layer and an auxiliary layer lasts 24-36 hours, only about 6-8% are auxiliary operations, i.e. the filter operates almost fully continuously, and the total yield of the thin layer filter, therefor, exceeds that of the column filter.

After the rebuilt Schüchtermann & Kremer-Baum suction filter operated satisfactorily with discontinuous knife adjustment, an old suction cell filter by Gröppel, Bochum, was rebuilt for thin layer filtration with a filter aid. This filter had about 8 m^2 filter surface, but only a very flat trough with very low submergence. Consequently, the trough had to be deepened to above the axis of the filter, which caused continuous leaks at the stuffing boxes due to the inaccurate roller bearings. The fastening of the filter cloth also had to be changed, because the filter was originally supplied with filter cloth. After overcoming these difficulties, the filter operates satisfactorily, the entire letdown produced could be processed. The filter aid consisted of a mixture of roughly 3.2 parts Kieselgur and 0.8 parts peat. Other materials have not proved satisfactory, because the application of the filter layer is already difficult. Moss peat has a surface similar to Kieselgur, consisting of siliceous shells, surrounded by a cross of fine siliceous hairs, which provides a particularly porus base. The large surface moss peat is coarser and has this particular disadvantage, that it isn't rigid, it sags in the heat and, therefor, cannot be used alone.

In detail, the following total thruputs were obtained with the rebuilt $8m^2$ filter in the short operating period still available.

Processed letdown	81873 kg.	
Thinning oil (from the application of the filter aid)	5500 kg.	(= 1.15%, of which
Filter aid, peat + Kieselgur	1100 kg.	(1025 kg. Kieselgur
	88473 kg.	
Filtrate obtained,	72501 kg	= 82.1%
Filter residue,	12500 kg	= 14.1%
Loss,	3472 kg	= 3.8%

The filter cake yielded on the average 35.0% L.T.C. oil when carbonized in the Fischer retort, compared to 34.5% from the column filter residue. The former, therefor, contains hardly any more oil than the latter. The bitumen obtained from the filtrate varied between 0.09 and 1.1% in its ash content after the apparatus has been thoroughly rinsed. Even the product topped in the tubular apparatus for a short time and then granulated in water contained only 0.21% ash, although the apparatus had not been especially cleaned. The filter, therefor, worked very satisfactorily with respect to purity of filtrate.

The yields obtained during this period cannot be directly compared with the results obtained at the start of the experiments at 300 atm. because the letdown, as measured in the test filter, had an average filter time about three (3) times as long, 6-9 minutes compared to 1-3 minutes. This deterioration in the filter time of the letdown was observed particularly with Saar and Ruhr coals. With Upper Silesian coal a deterioration in filter time was also observed, which was partly due to the unfavorable temperature distribution in the four (4) converters. The three (3) and four (4) converters could not be maintained at the same temperature as converters one (1) and two (2), in which the main conversion takes place with consequent greater heat of reaction. From experience it is better to have the temperature rise towards the end of the reaction system, so that sufficient conversion will take place even in the last converter, in spite of the decreasing H_2-concentration.

In order to equalize the deteriorating filter yield, the filtration temperature was once increased from 130-140 to 180°C, which increased the yield to 100-120 kg. This was made possible by increased cooling of the lines to the vacuum pumps, whereby the vaporized oil could be better condensed and recovered. Furthermore, a further increase to 160-180 $kg/m^2/h$ could be obtained by increased cutting off of the cake, i.e. an increased consumption of filter aid, whereby the former yield with letdown from 300 atm operations could almost be reached again. Again, the operating period could be increased from 36 to 60 hours by using a thicker auxiliary layer, so that only about 5% of the total filter time needed to be used for the three (3) hour period of rinsing and reapplication of the filter layer. In periods of normal cake removal the filter aid consumption therefor, dropped to 0.3 to 0.4% of the processed letdown.

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Comparison with Column Filter

The same letdown was run in column filters at the same temperature. The yields, at first, were about 220 kg. with undiluted letdown. With the letdown diluted 1:0.25 the yields rose to about 300kg for a short time, or about 120 kg for the entire filter. However, these yields could be obtained for only about four (4) days. The filter time then dropped sharply to about 60 kg in 10 days, i.e. to one fifth. After 18 days the ceramic filter base had to be replaced, after a total of roughly 26000 kg/m^2/h had been put thru it. Since one of these filter base inserts weighs approx. 360 g and abt. 85 pieces are required for 1 m^2, roughly 0.15% of the letdown was consumed in filter bases. Based on weight, the filter base brick consumption is, therefor, not quite as great with decreasing yield. If the starting yield is maintained, which is the case with the thin layer filter, the filter brick consumption will be just as great, by weight, as the filter aid consumption with the thin layer filter. The cost of the brick, however, is much greater. One m^2 filter brick costs roughly RM. 90.00 without binder and installation, or about RM. 100.00 installed. By comparison, 1 m^2 filter aid for the thin layer filter costs only RM. 3.50-4.00, i.e. the filter brick costs about 26 times as much per m^2 as the filter aid. This great advantage could only be overcome, if it were possible to regenerate the brick, which we have not been able to do up to the present. On the other hand, the cost of the filter aid can presumably be still lowered by using different materials. Since the thin layer filter, in its present form as vacuum filter, works almost fully continuously, needs almost no attention, is very simple and safe, and produces at least the same yields, while the extensively mechanized column pressure filter is a very complicated and costly apparatus, considerably more expensive to operate, the comparison favors the thin layer filter, by far.

The development of the thin layer filter is not complete. In the transition to the pressure filter the same progress must be made which characterizes the column filter as pressure filter, particularly the use of higher temperatures, which in vacuum, is limited by the evaporation temperature. Increasing the pressure alone beyond a certain figure does not cause any appreciable improvement, because the porosity of the loosely applied auxiliary layer is reduced thereby. The progress achieved to date with the 0.2m^2 vacuum filter built into a pressure tank has been unimportant. The reason for it is this, that the control head built for vacuum cannot be kept tight against pressure and continuously blows off (leaks). The filter must, therefor, be rebuilt before further experiments can be made.

On the other hand, great progress is to be expected from the careful removal of the letdown from the high pressure vessel, particularly at high pressures. With easily filtrable letdown the filter yield is doubled, with letdown difficult to filter it is even trebled. This means a longer life for the filter bricks and decreased consumption of filter aid with thin layer filters. In future planning special procedures must be developed for careful withdrawel of the letdown from the hot catchpot

Supplement to Report of 23 July 1942.

By Pfirrmann, Ludwigshafen, 24 July 1942.

The results obtained with three (3) different coals, Upper Silesia, Ruhr and Saar, in the 8m^2 filter show some differences in that Upper Silesian coal is more readily filtered than Saar and Ruhr coals.

These differences are not at all dependent upon location but are due to differences in the quality of the coal. Upper Silesian coal, by far the easiest to filter, is a young coal rich in bitumen. The somewhat more difficult to filter Saar coal is closely related to it. It is only a little older (less O_2-content) and contains slightly more volatiles, but twice as much ash, with consequent smaller conversion and considerably more filter residue, i.e. the letdown is more difficult to filter. Ruhr coal is much older and, therefor, poorer in conversion and filtration. The factors which influence filtration are again summarized in the following table:

Kind of Coal	Volatiles	C	O	Ash	Conversion	Comparative Filtration
Upper Silesian K-1242	37.6	81.9	11.0	4.9	92.8	Best
Saar K-1246	40.9	82.4	9.2	9.2	78.4	Average
Ruhr K-1247	33.3	85.0	7.5	4.4	73.4	Worst

When operating with middle oil and less H_2, the rule obtained for 300 atm, that conversion and filtrability are closely related to the age of the coal (O_2 or C content) and that with equal ash content the coal is better filtrable the younger it is, is also valid here. Consequently brown coal is generally the best to filter, conversion is as high as 98%. The ash content reduces conversion because it is impossible to bring the unconverted coal below the percentage of ash. With higher ash content, the unconverted residual coal content in the residue even rises sharply, which is probably due to the diluting effect of the ash. The same thing is true of extraction with tetraline without H_2, where I have experimented with it.

If we, therefor, compare the filtrability of the letdown obtained by various processes, it is sufficient to compile the data for a kind of coal of a certain composition, independent of its origin. We can then predetermine the behavior of coals of other composition within wide limits.

The attached diagram attempts a graphic representation of the filtrability of bituminous coals varying in volatile content between about 40 and 25%, with an ash content of roughly 4%.

About the same relation exists in the conversion of a coal of 40% volatiles but increasing ash content. The filtrability erd also steadily drops with increasing ash content, approximately following the same curves. The diagram shows the influence of the operating method. The easiest to filter is the extract obtained with tetraline cresol, with yields of 500 and above. About the same yields are obtained if the coal is pasted with approximately double the quantity of middle oil and no letdown is recycled, which is possible only in discontinuous operation. With letdown recycling and 1:1