T.O.M. Reel 273

UNITED STATES BUREAU OF MINES

TRANSLATIONS

by the

Coal Hydrogenation Demonstration Plant,
Louisiana, Missouri

T-202 to T-360

The following translation number is omitted: T-356.

001 45

TOM Reel 70
Fr: 000642-47

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

T-202

KCBraun
1/2/47

PRESSURE STABILIZATION OF CATCH-POT PRODUCTS WITHOUT INTERMEDIATE EXPANSION AND RICH-GAS COMPRESSION

Dr. Kurt Wissel, Stettin-Pölitz,
1 Dec. 1944

After the last attack the condition of our plant was as follows:

The H_2-production, including washing and compressors, had suffered heavy damages, though a partial resumption of operations in these departments was possible within the near future. The high pressure operations were also damaged, but the damages could be repaired in a short time, at least in some stalls. However, the distillation and intermediate tank storage, as well as gasoline scrubbing, stabilization and rich-gas production were in such a condition that they could not be repaired within a short time. Only 3 of the 39 tanks in the intermediate tank storage for vapor phase and catch-pot products were undamaged and one of them could be used in part. Of the 8 distillation units, 2 could be repaired within a month, 4 in 6 months, and the remaining 2 in 9 months. The rich-gas system was out of service for 2 months and the liquid gas production could be resumed at about 30% within 2 months and about 60% in 5 months, if the hygas compressors could be repaired in the same time.

From this condition, particularly the almost complete destruction of our processing facilities following hydrogenation, it was evident that a resumption of normal operations with our present methods could not be expected for several months. We, therefore, sought and found a way which promised resumption of operations within 3 weeks by improvization. We decided upon an entirely new method of operation by borrowing pressure tanks and steam distillation units from other less severely damaged departments for our vapor phase and DHD plants, such as the containers from the L.P.G. storage and the pressure stabilization unit from the T-52 plant.

Before showing the new method, let us take a look at the old one, shown in Fig. 1. The let-down from the prehydrogenation and gasoline stalls was formerly decompressed into the dewatering tanks by way of the socalled ant eggs (elliptical shaped pressure vessels) and the gasoline was cut out in the stills. While this gasoline, after scrubbing in caustic soda and water, was stabilized, together with the C_5 and higher hydro-carbons from the rich-gas decomposition, and the attendant propane and butane hydro-carbons went to the L.P.G., the rich gases from the liquid and vapor phase were processed together in a separate operation, shown in Fig. 3.

The rich gas is first compressed to 5 atm. Then, after an alkacid wash at this pressure, it is compressed to 25 atm. in a second stage. The attendant condensate, together with the condensate from the first stage, is distilled at 25 atm. After driving off the methane and ethane, the liquid product is scrubbed with caustic soda and water and decomposed in a second column at 18 atm. into L.P.G. ($C_3 + C_4$), C_5 and higher hydrocarbons.

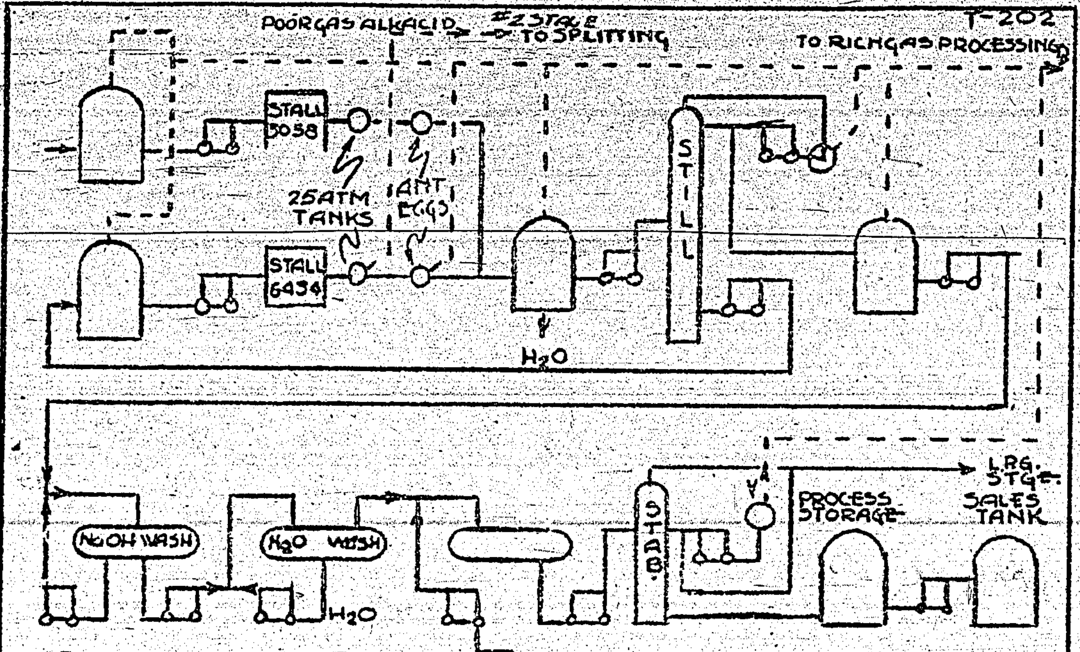
In the new method, shown in Fig. 2, the let-down is no longer decompressed to atmospheric pressure, but is conveyed by the pressure directly from the 25 atm. expansion tanks into pressure containers of 150 m^3 capacity, formerly used as L.P.G. containers. In these L.P.G. tanks the water is separated from the product, the ammonium sulfide-ammonia water is removed with a container pressure of 14-18 atm. absolute and the product free of water is stabilized at its own pressure in pressure columns (butane separation unit of the T-52 plant) and then conveyed under pressure into the steam heated distillation unit of the DHD-II plant without an intermediate container. From there, the gasoline is drawn off as finished product without an intermediate container over caustic soda and water scrubbers and an after-stabilization. The supplementary scrubbing with caustic soda and water and the stabilization of the gasolines produced from the let-downs after the let-down stabilization and separation in the re-distillation was necessary, because a complete stabilization of the vapor phase let-down could not be obtained at high thruputs with the limited plant facilities available.

On the contrary, we are better able to use this process with the let-down from the DHD stalls in available similar apparatus, due to the higher gasoline content in the let-down. A supplementary washing and stabilization of the DHD gasolines produced is not necessary here for the products from pressure distillation.

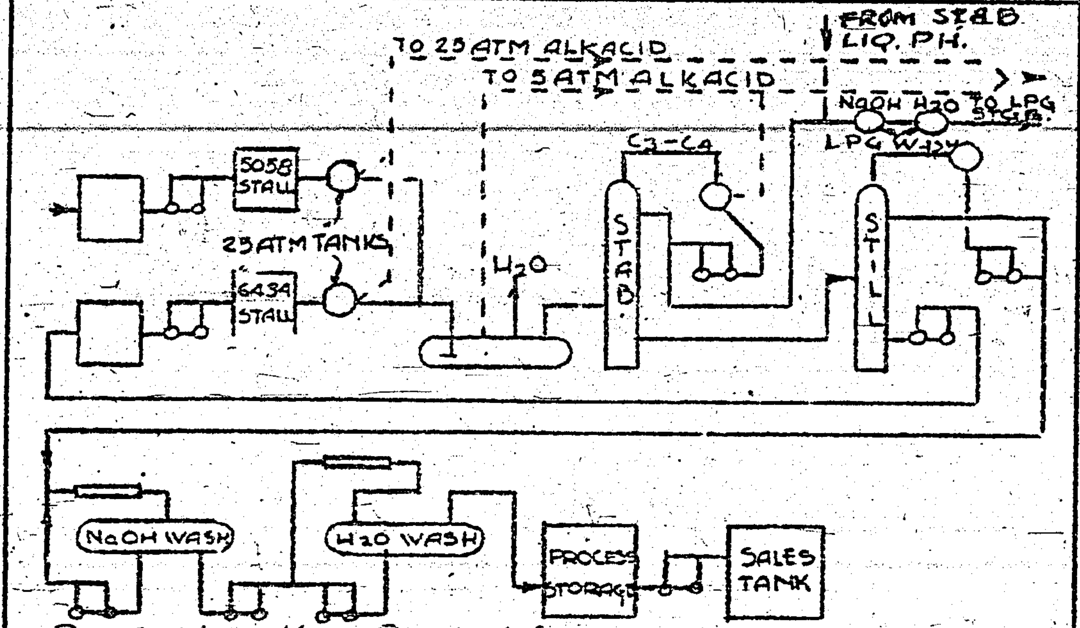
Attention should be called to one thing. When available apparatus is used for stabilization of vapor phase products these should first be freed of iron oxyde by flushing with acid. If this is not done, iron sulfide will be formed by the hydrogen sulfide in the let-down which may cause all kinds of trouble.

In a comparison between the old and the new method it must not be overlooked that the old method, with its extensive plant and large tankage, permitted greater elasticity in production and better control of the maximum yield, particularly with reference to the large number of raw products processed in Pölitz. No storage in process is available with the new method because of the arrangement of the various units without intermediate tanks, and it must, therefore, be expected that the whole plant may be shut down in case of trouble anywhere. Since in the new method finished products are produced in 5-6 hours an even stricter analytical control of operations must be had in order to produce satisfactory products, because it is very difficult to mix the products to obtain a satisfactory test. Of course, all of the hydrogen sulfide in the let-down product will appear in the liquid gas from the let-down stabilization and in the residual gas from the pressure let-down. The liquid gas must, therefore, be scrubbed before delivery, which requires more caustic soda than in normal operations. Experiments have already been made to scrub the liquid gas with alkacid. With an L.P.G. containing 20 g H_2S/1 the following results were obtained by scrubbing with alkacid lye: with 1 vol. alkacid lye/1 vol. L.P.G., 99% of the H_2S was washed out, with 1 vol. alkacid lye/3 vols. L.P.G., 98% of the H_2S was washed out. However, the new method has this advantage, that it requires fewer L.P.G. distillation units, pumps, tanks, and smaller gas lines. In addition, the processing of the rich gas is eliminated in the vapor phase and the DHD plant. The decreased space taken up and consequent decreased quantity of oil in process, as well as the underground storage in the L.P.G. containers used as intermediate tanks, provides greater safety against bombing attacks. This method is also especially suitable for underground storage because of the appreciably smaller space required. This method has enabled Pölitz to obtain a relatively high production of quality VT and DHD gasoline in a short time. In the direct stabilization 70-85% of the L.P.G. present was immediately obtained in a liquid condition. The residual gas produced under pressure causes no condensation in the lines, because of the absence of C_5 and higher hydro-carbons due to the removal of the greater part of the propane and butane contained in it. The content of free ammonia in this residual gas is extraordinarily small, because the water is separated from the let-down under pressure. This makes it unnecessary to scrub it in order to remove the residual ammonia. The introduction of steam distillation units into the vapor phase, instead of the gas fired stills, has greatly simplified operations, because the starting-up time of 2 hours for the steam stills compared to 15-24 hours for the gas fired stills makes the plant always ready to start operations, and fluctuations in thruput are taken up by the automatic regulators.

The new method has now been operating successfully for 6 weeks in the production of DHD gasoline and for 4 weeks in the production of VT in the vapor phase. The catch-pot products from the liquid phase could be processed in a similar manner, if the corresponding apparatus and power installations were available in the plant. Fig. 4 shows the proposed new method.



Processing Vap Ph. Letdown Old Method
FIG. 1



Processing Vap. Ph. Letdown New Method
FIG. 2

T-202

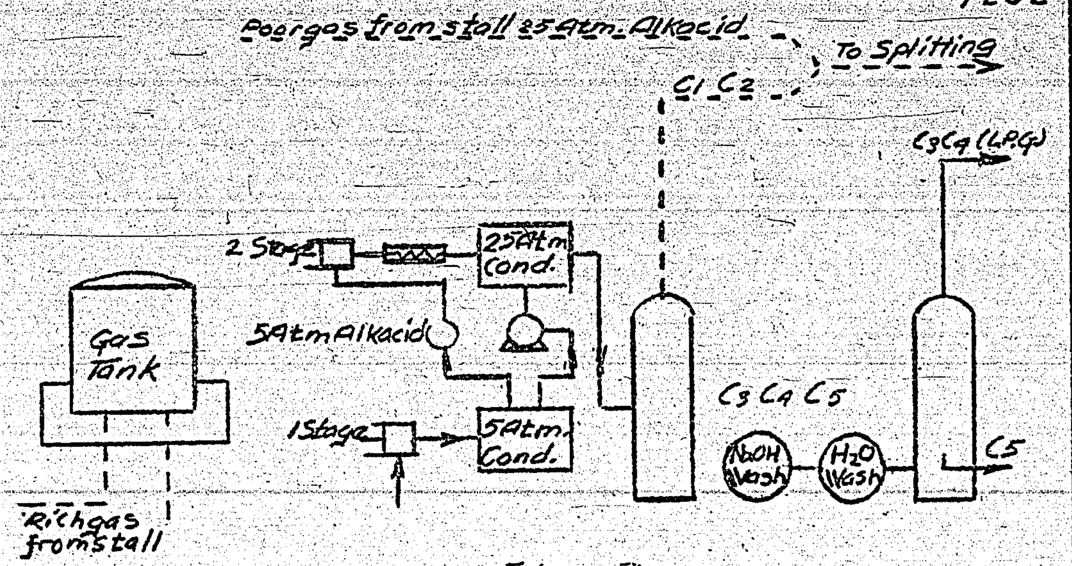


FIG. 3

Richgas Decomposition Liq&Vap.Ph. Old Method

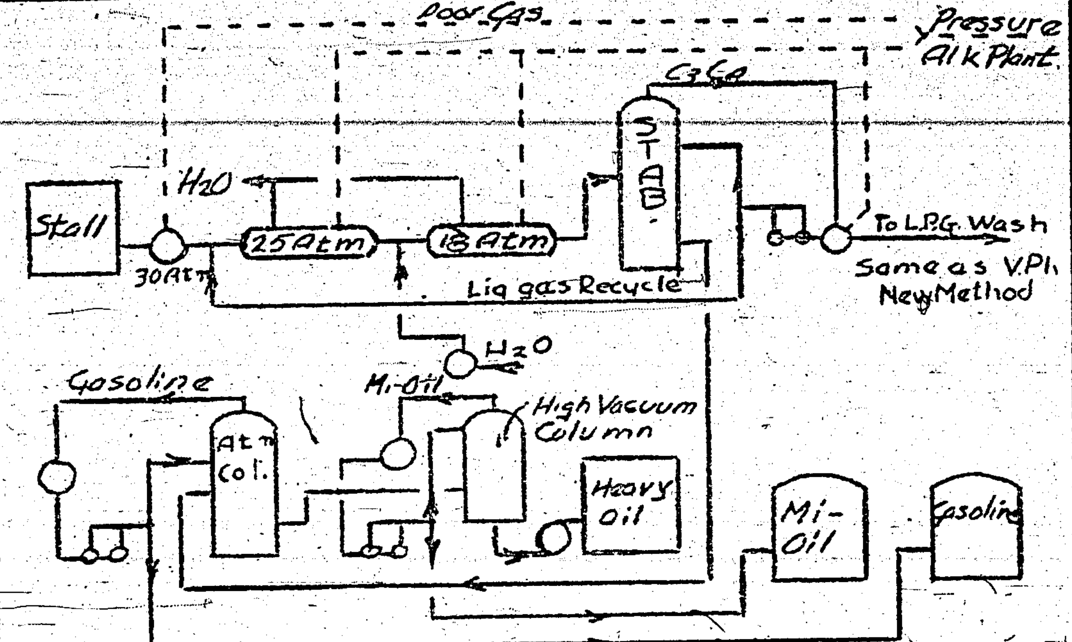


FIG. 4

Processing Liq Ph. Letdown New Method

TOM Reel 130,
Ref. m-8
Pp. 158-166

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

T-203

TROUBLE DURING OPERATION OF HYDROGENATING PLANTS.

(From the Leuna Reports for 1937 - 1938)

This naturally is not a complete list, because trouble during operations frequently result from very complicated causes, which are difficult to diagnose.

1. The density recorder no longer records the density of the outlet gas. A number of throttling disks are installed in the pipe line to the density recorder, to throttle down the pressure. The reason for the interruption is the plugging up of the orifices.

a. This may happen because of foaming in the liquid phase, which will cause some material to be entrapped and carried through the pipe line. One must first attempt to blow through the orifices in the pipe line, i.e. an exhaust valve in the density recorder is opened.

b. The level in the catchpot has become too high. The accuracy of the level readings must be checked. The level tube is replaced and the level is again read off to see if the reading was correct. When there is much foaming one may observe foam entering the level glass from above, but a slight foaming will not be directly observable. Higher temperature at the outlet is a remedy (also reducing somewhat the amount of cooling water). It may be mentioned here that a tar stall is more likely to foam, than a gasoline stall. The catchpot in the tar stall must always be sufficiently large.

2. The outlet gas flow meter does not register correctly. The valves to the meter are first closed and the by-pass opened. The pots are then drained into the measuring pipe line. Should a wrong reading be again obtained, we shall have again to assume that some of the feed to the cold catchpot reaches the gas line. (This would also be indicated by the density recorder, if connected, because it is more sensitive).

Remedies: The level in cold catchpot is lowered or the temperature raised (it naturally may happen that the foaming is so strong, that these measures still be found inadequate), and the injection reduced. It would be possible in case of need to operate with no flow meter.

3. The gas inlet flow meter indicates a reduction in the amount of gas going in, and the pressure difference in the stall rises. If the pressure difference would not increase, one would first drain the pot into the measuring pipe line.

Should, however, the pressure difference rise while the amount of gas is reduced, one will have to assume that the level in the cold catchpot is much too high (which may have not become noticed because of the plugging up of the level glass), and as a result, the feed is being thrown up high into the gas line by the gas. This results in a large resistance: the reading of the pressure difference indicator will be high. The pressure in general will have risen as well, and this becomes manifest in a smaller intake.

4. All the gas instruments in a stall give faulty indications. (Liquid phase). This means the inlet and outlet flow meters, level indicators, cold gas flow meters, etc. This indicates that the scrubbing oil is being entrained from the scrubber. It was principally foam, because it had passed the gas circulation pumps and the catchpot. The scrubber must be immediately checked (scrubbers most likely overloaded), and the principal measuring instruments again put in operation. This trouble has once happened in the I.G. as follows: The hot catchpot bottom of one of the stalls was carried over, the wash oil immediately reacted with it, began to foam and boil over.

5. The sp. gr. of the cold catchpot is changed, and becomes either higher or lower, which may result from changes in the injection feed.

The sp. gr. increases:

This may be caused by:

a. Too low a temperature;
b. A very great change in the amount of gas. (Remark: When the injection feed is reduced, say to one half, while the amount of intake gas remains, the same, the temperature must be somewhat lowered to keep the specific gravity unchanged. (Remark in pencil: In this case the sp. gr. would rise).

c. Reduced activity of the catalyst; this may happen if water is injected with the injection feed, in which case the temperature as well will drop;

d. A short circuit in the heat exchanger. This will not necessarily be made evident in the vapor phase by a change in color. In the liquid phase, 0.5 - 1.0% fresh feed will cause a strong discoloration. When the sp. gr. keeps rising, or the discoloration becomes more prominent, one may pretty safely blame the heat exchange. The pressure difference will finally become lower.

The discoloration and the changes in specific gravity may, however, be also caused by other reasons, namely the overflowing of the hot catchpot. For this reason, the two level gauges are re-set, and the hot catchpot again emptied until gas escapes from below. Should the crude catchpot product still indicate dirt, a reduction in the size of the hot catchpot as well as a short circuit in the heat exchanger must have occurred.

When solids appear in the catchpot, care must be taken, because the pressure release valve will soon become worn out. This is the reason why today needle valves are installed here with seats of Dura metal; in addition they are made replaceable.

6. <u>The two level indicators give different readings.</u> This may be caused by:

a. The pen may be stuck;

b. Oil in the pipe line of the indicators on the catchpot;

c. The pipe line of the level indicators has become plugged up.

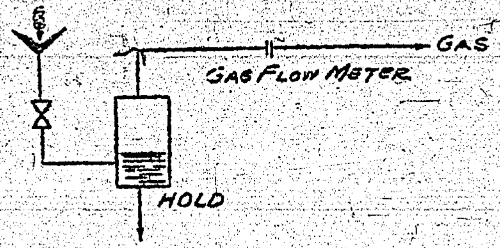
d. The level tube itself is plugged up;

In cases like this, the indicator pipe line must be again flushed with gas, or with oil, if the gas has not helped (a small hand pump must be placed near by).

7. The level of the hot catchpot is continuously kept high, but gas never the less escapes with the HOLD.

Coke becomes deposited in the hot catchpot, creating eddy effects (Leuna "bathtub effect") which entrain gas.

The large amount of entrained gas is established on the gas gauge of the pressure release pot.



8. One of the level indicators does not register at all. The by-pass valve may be leaky; the long measuring tube may be torn off.

9. The outlet gas flow meter and the pressure difference gauge give higher readings. Find out if the amount of cold gas has been greatly increased. If such is not the case, the gas inlet flow meter is probably out of order, and the operator of the regulator valve has opened the latter too far. (The inlet gas flow meter reads therefore too low). It may happen then that some of the contents of the sump phase is forced into the hot catchpot, and the level will rise very much.

Apparently this happens rather frequently; the operator at the inlet valve must therefore be carefully on the watch.

10. Too much gas is given off when the pressure is released from the catchpot product. Reasons: The level in the catchpot is too low, an eddy effect is produced and gases are carried over. When the level reads correctly, this effect may be avoided by keeping the level in the upper gauge within the glass. It naturally may also happen, that the level gauge is wrong, as a result of plugging up, foaming, or optical illusions.

11. Injection pump does not inject sufficiently. Frequently caused by sticking of the suction valve,

12. It may happen with two middle oil pumps in parallel, that when one pump is shut down, the second pump, which is kept running, does not supply a sufficient amount. This is the result of a failure to isolate the surge tank on the pressure side of the shut-down pump. The N_2 in this vessel may then become exhausted through the pump (especially with a raised suction valve) into the suction line, and thus reach the second pump.

The valve in the suction line of the shut-down pump may never be closed before releasing the pressure on the pressure side, including the surge tank.

13. <u>The productivity of the hot circulation pump drops.</u> May be caused by the gas, or by a drop in the pressure of the fuel oil system.

012 6

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

T-204

KCBraun
1/3/47

PROCESS FOR DE-ASHING LIQUID HYDRO-CARBON FUELS.

German Patent 722406

Class 12o, Group 1_{05}

18, Sept. 1936

Issued to

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

by

Dr. Mathias Pier, Heidelberg and

Dr. Walter Krönig, Ludwigshafen, Rh.

The processing of liquid or semi-solid pressure hydrogenation or extraction products of substances, such as coal, oil shale or peat, has been found very troublesome, if these substances contain ash in solution or so finely dispersed that it can not be removed by mechanical treatment, such as filtration, centrifuging or sedimentation. This is particularly disadvantageous, if the substances are to be subjected to pressure hydrogenation or splitting in the presence of a catalyst, where required. For example in passing the liquids to be processed over catalysts at high temperatures, the ash is retained on the surface of the catalyst causing premature deterioration of its catalytic effectiveness. It has further been found, that if oils of this kind are used for the pasting of coal for pressure hydrogenation or pressure extraction; the ash may, for example, by itself or in combination with the ash from the coal to be processed, be separated and collected in the reaction vessel, at timesin comparatively course form, and thus reduce the useful reaction space.

It has now been found, that de-ashing may be obtained in a simple manner, if the substances under discussion are treated with CO_2 or ammonium carbonate at high temperature in the presence of water, preferably under pressure. About 0.2 to 10% water, based on the quantity of oil to be de-ashed, is used for this purpose. When so treated, the ash in solution or fine dispersion assumes such a coarsely dispersed form, that it can then be removed without difficulty by mechanical means, such as filtration, centrifuging or sedimentation.

For example, the oils to be treated may be treated directly with solid ammonium carbonate and the water added separately, if it is not already present in sufficient quantity. But the oils may be also mixed with a watery solution of ammonium carbonate. When CO_2 is used alone or combined with ammonia gas, pressures of from 5 to 100 atm. have proved advantageous. The temperatures to be used range between 100 and 400°C. The additional use of H_2 is recommended in order to avoid an undesirable decomposition of the oils. The pressure hydrogenation and extraction products may also be treated in the prescribed manner directly after their production, while they are still hot, as, e.g. on the cooling run from the reactor.

Compared to the use of H_2SO_4, as used in the de-ashing of tars, the process herein described has this advantage, that no losses occur due to the formation of acid resins. In the known process a pitch like viscous mass is produced, which is not the case in this process. In the well known use of an alkali-humate solution, also, concentrated H_2SO_4 is added, causing losses due to the formation of acid resins. Furthermore, the process described herein uses simple, inexpensive media, which separate by themselves and cause no pollution of the material to be processed.

Example 1.

Middle German brown coal is pasted with oil and subjected to pressure hydrogenation in a high pressure converter in the presence of an iron catalyst at a pressure of 200 atm. and a temperature of 465° C. The reaction material from the high pressure converter is conducted to a hot catch pot, from which the sludge (let-down) is drawn off at the bottom and the reaction product, consisting of gasoline, middle oil and a part of the heavy oil, together with the hydrogen, is drawn off at the top. From this reaction product, the heavy oils boiling above 325° C are separated by distillation and then added to the let-down (Abschlamm). The mixture of both is then centrifuged, producing a centrifuge oil containing 2.7% ash, which will pass thru the finest filters.

To this centrifuge oil containing ash is then added 5% water in the presence of a mixture of H_2 and CO_2 at a pressure of 75 atm, where the partial pressure of the H_2 is 40 atm. and that of the CO_2 35 atm., and the mixture heated for 30 min. to 340° C. In the subsequent filtration an oil containing only 0.1% ash is obtained.

If the centrifuge oil containing ash is mixed with 10% ammonium carbonate and 3% water and heated for 1½ hrs. to 310° C in a closed vessel @ 5 atm., the filtered oil will contain 0.3% ash.

Example 2.

An extract containing 0.7% unfiltrable ash and derived by pressure extraction from rhenish brown coal with the use of tetrahydro-naphthaline is stirred for 24 hours at normal pressure and heated to 130° C, together with the extraction medium (80% extract and 20% tetrahydronaphthaline) and with continuous injection of CO_2, ammonia and steam. The tetrahydro-naphthaline being evaporated in this operation is constantly replaced. The liquid is then filtered @ 180° C and the filtrate freed of the tetrahydronaphthaline. The extract derived by this method contains only 0.1% ash.

Patent Claim.

Process for de-ashing of liquid or semi-solid products of pressure hydrogenation or extraction from substances such as coal, oil shale or peat, characterized by treating these substances at increased temperature and preferably under pressure with CO_2 or ammonium-carbonate in the presence of water and separating the coarsely dispersed ash therefrom by mechanical means.

TOM Reel 178
Pp. 1491-1509
& TOM Reel 165
Pp. 465-498

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

T-205

KCBraun
1/6/47

AMMONIAKWERK MERSEBURG, G.m.b.H.

LEUNA-WERKE.

(Abstract).

The Leuna Works are located about 20 km South of Halle a.d. Saale, on the railroad line between Berlin and Frankfurt/M. The plant is a subsidiary of Interessen-Gemeinschaft Farbenindustrie; A.G. (I.G. Farben), Frankfurt/M. It is one of the largest chemical plants in the world and covers an area 3.5 km long by about 1.3 km wide.

The plant was built by the Badische Anilin u. Soda Fabrik, Ludwigshafen/Rh. in 1916 and started operations in April 1917. It received its name from the small village of Leuna, within the boundaries of which it is located. Its original purpose was to make nitrogen for agriculture and munitions by the Haber-Bosch process, developed by B.A. & S.F., which takes the nitrogen of the air for use as required. It can produce 860000 tons/ann. of nitrogen in the form of ammonia (prewar).

The plant was located at this particular point because of its strategic location in the heart of the Central German industrial and brown coal region, offering good transportation facilities and an abundance of the principal raw materials required for the ammonia synthesis, coal and water, the latter pumped from the Saale, 2 km away.

In 1923 the manufacture of methanol was taken up. Methanol or methyl-alcohol, was formerly made from charcoal and therefore called wood alcohol. It is the basic material for many chemical processes, particularly for the manufacture of formaldehyde, which is an important raw material for the synthetic resin industry. The capacity of the plant for producing methanol has been increased from 30000 tons/ann to about 150000 t/ann during the war.

In 1927 gasoline production was started. This enabled Germany to produce a part of its motor fuel requirements from domestic raw materials, such as tars, oils or brown coal by pressure hydrogenation. The original installation of 100000 t/ann has since been enlarged to produce over a half millon tons per annum.

Besides these three major products, Leuna also produces a variety of other products, and by-products, such as isobutyl and propyl alcohols, ethylene, phenol, fatty acids, cleaning compounds, sulfur and others, whose combined production runs well into six figures, expressed in t/ann.

At the end of 1933 Leuna Werke employed about 9000 workers and 1750 salaried employees. The manufacturing operations are carried on in over 850 buildings of various sizes, covering a built-up area of upwards of 150 acres, including hydrogen production and power plants.

The steam required for these various operations is produced in 95 tubular boilers with a total heating surface of 60000 m^2 in 7 boiler houses (Prewar figures). The approximately 20 trains of coal per day required to produce this steam is supplied by the company's own open-cut mines over a company owned standard gauge railroad about 20 km long.

The power plant has a nominal capacity of 82000 KWh. The power distribution system consists of 520 km cable lines and 37 substations. (Prewar figures).

The water works is located about 2 km away near the village of Daspig on the Saale. The capacity of its pumps is over 24000 m^3/h, (prewar figure), which corresponds to a water requirement of a city like Berlin. Most of the water is used for cooling purposes and is returned to the river after repeated use and cooling over huge cooling towers.

The works also includes many buildings, ~~[illegible]~~ repair shops, welfare institutions such as emergency hospital, modern bath houses, dining rooms, etc. as well as office buildings, lecture hall and laboratories.

TOM Reel 163
Pp. 110-113

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

T-206

KCBraun
1-7-47

PROCESSING OF LET-DOWN BY FILTRATION

By Pfirrmann, Lu, 19. October 1942
(See also T-177)

The complete separation of the solids in the let-down from the valuable products of hydrogenation and the latter's most effective recovery is possible only by filtration.

Unfortunately, only let-down produced by one distinct operating method can be processed by filtration. The conditions necessary for a filtrable let-down are summarized in the following:

Pasting with a middle oil rich in aromatics, limitation of the hydrogen consumption and consequent hydrogenation, producing a largely bituminous hydrogenation product, a low thruput (below 0.4 t/m³ converter vol/h) at low and medium pressures, and a heavy oil return as low as possible. This applies to pressures up to about 450 atm. If the pressure is increased to 700 atm. the operating conditions can be extended. The middle oil pasting remains the same, but the hydrogenation temperature can be increased to 470-480°C and the thruput increased to 1.0 t/m³ converter vol/h. The hydrogen consumption can also be increased, so that, besides the bituminous hydrogenation product, a greater proportion of liquid products, gasoline and middle oil, is produced. This operating method at 700 atm., therefore, represents an intermediate stage between hydrogenating extraction and normal hydrogenation, whose let-down is still practically unfiltrable.

The filtration itself is fitted to the characteristics of the filter feed. Since the solid particles are much reduced in size in the hydrogenation process, filtration can not be done thru a thick cake of solid particles, but the cake must be constantly renewed. The filter bases should be made readily interchangeable, because parts of the hydrogenation bitumen become insoluble by further polymerization at the high filtration temperature of 150-200° C necessary and the filter bases become caked by lac-formation.

The best type of filter has been found to be the "thin layer filter" by Dorr, with a layer of "filter-aid" of Kieselgur or other porous material, which is automatically removed with the filter residue. The pressure column filter (Druckkerzenfilter) by Jung can still be used at these high temperatures, but requires more time for the auxiliary operations and is more complicated and expensive. In particular, the ceramic filter inserts are readily fouled, due to the formation of lac by hydrogenation bitumen. The use of column filters might be considered, if the ceramic filter inserts could be readily regenerated.

The thruputs obtainable with a "thin layer filter" at 300 atm. are about 240-280 kg/m^2/h, at 700 atm. about 150-180 kg (under special conditions even 200-250 kg). The ash content of the filtrate is only 0.006 to 0.04%, so that only about 0.1%, or less, of ash is contained in the bitumen free of solvents. The filter residue contains 35-40% oil, largely easily distilled middle oil. It can, therefore, be rapidly carbonized (Schwelen) with little loss.

The advantages of let-down processing by filtration, compared to the formerly usual methods of centrifuging and low-temperature carbonization, are obvious. The carbonizing department (Schwelerei) is relieved, because only the solids proper need be processed and not the large quantity of heavy oil contained in the centrifuge residue. The carbonization losses are, therefore, smaller and the carbonization process itself simpler, so that it can be done in brick ovens, inexpensive to build and operate. In addition, oil free of solids, which, due to its characteristics, can even be hydrogenated under the worst conditions, is returned to hydrogenation, so that gasification could be further reduced.

The particular operating method required to produce filtrable products yields about as much electrode coke (32%) at 700 atm. as oil (34%), if it is desired to make electrode coke from the hydrogenation bitumen. It is to be expected that with the further development of this operating method the proportion of oil can be considerably increased, so that filtration may also be applied to fuel oil or gasoline + middle oil, respectively, even with a modified operating method. Then the goal of complete utilization of coal will have been reached by utilizing the C-constituents in the ash of the carbonization residue, worthless today, in the form of valuable electrode coke.

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

T-207
KCBraun

INSTRUCTIONS FOR MEASURING THE PRESSURE DIFFERENCE IN A HIGH PRESSURE STALL

By Dr. Frese, Jan. 8, 1947.
(See Attched Sketches).

The pressure difference is measured to control the stall and should be done:

a. In normal operations at regular intervals.
b. When the resistance in the stall increases, as indicated by the pressure recorder in the control room.

A satisfactory measurement can only be obtained, if it is done quickly from a central instrument board, on which pressure gauges from all the lines are located. This should be near the stall wall, on the outside.

All measuring points or lines conveying solid substances should be constantly flushed with a small quantity of flushing gas or oil; see measuring points II, III, IV or V. A back flow of coal paste must be avoided by all means.

All lines should be heated and insulated between the valve group and the measuring point.

Measurements are made in the following manner:

1. Position of Rest.

Valves 23, 24, 25, 26, 32 and 33, as well as all "c" valves are closed. Valves "a" and "b" are also closed, with the exception of groups II, III, IV and V, which are flushed with gas during operations. Valves B, P, 3, 21, 22, 27, 28, 30 and 31 are open.

2. Measurement.

a. Before starting the measurement, close the "a" and "b" valves of groups II to V, inclusive.

Slowly open valves 23 and 26 a little and flush thru the open valves 27 and 28.
Slowly close valve 28.
Slowly throttle valve 27 and close when operating pressure is reached, then fully open valves 23 and 26.
Close valve S.
Open all "c" valves.

b. Blow out the "c" valve of the line to be measured by a rapid successive opening and closing of the respective "b" valve.
Close the "c" valve of the line to be measured.
Open valves "a" and "b" of the line to be measured and close valves 30 and 31.
Close valve B.
Open valve S.
Turn on and read current from differential pressure indicator.
Close valve S.
Open valve B.
Close valves "a" and "b" of the measured line.
Open valve "c" of the measured line.

c. After 2b), above, measure points I to X, inclusive.
Reverse by closing valves 23 and 26 and opening valves 24 and 25.
Then, after 2b), above, measure points II to IX, inclusive.

3. Shut Off.

Close all "a", "b" and "c" valves.
Close valves 32, 33, 24, 25 and 26, 23.
Open valves B, P, S, 21 and 22.
Slowly open valve 27 and de-compress.
Slowly open valve 28.
Open valves 30 and 31.
Open valves "a" and "b" of groups II, III, IV and V for injecting flushing gas.
Turn off the gauges used in the measurement.

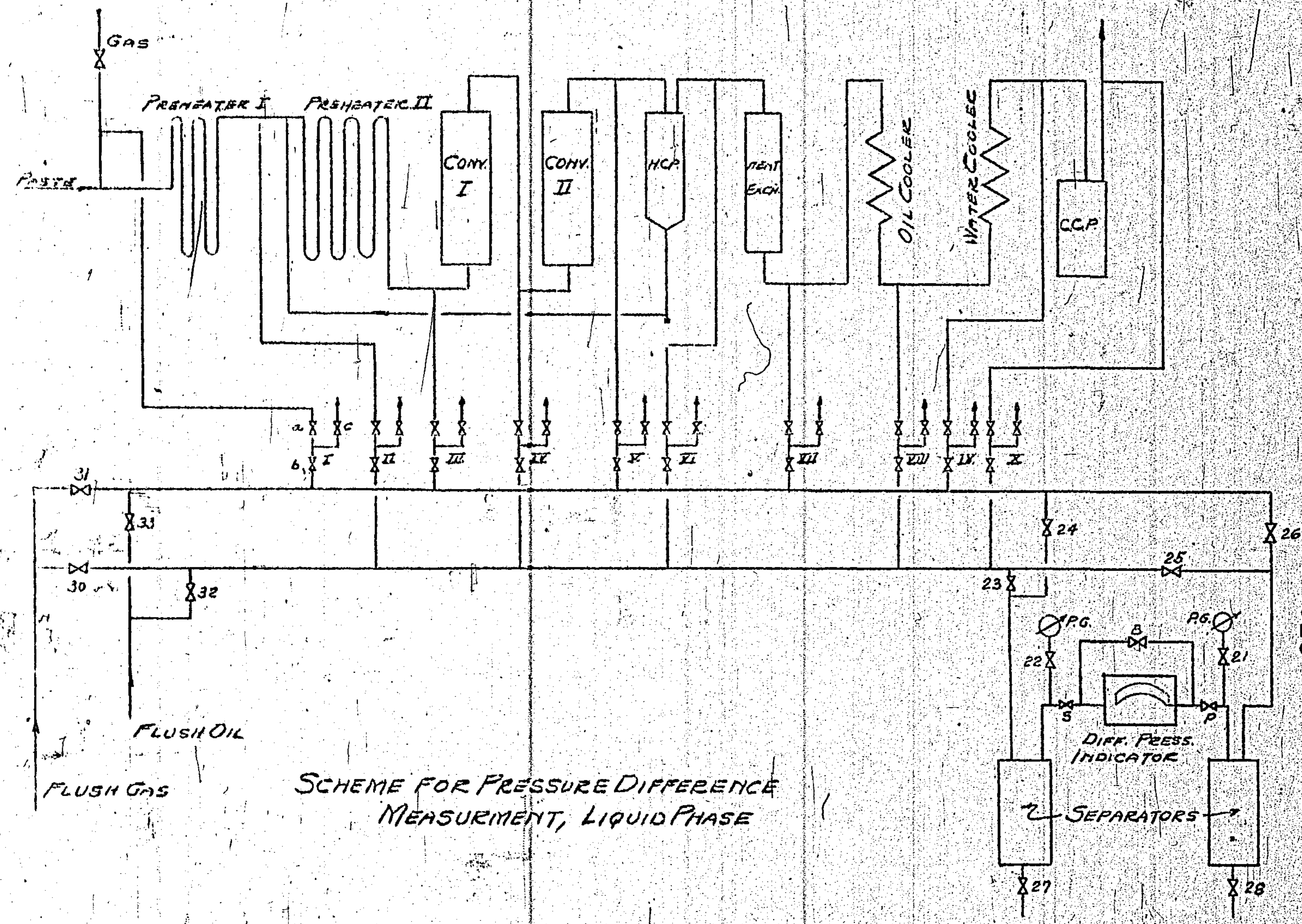
REMARKS:

If the equipment is serviced properly, there will be no trouble. By all means avoid a back flow of oils containing solids. This not only causes plugging of the measuring lines, but may also cause wear in valves "a", "b" and "c", so that they may not close satisfactorily, which, in turn, may decompress the stall thru these valves and cause fires.

In putting a stall into operation, it may happen that the small throttling orifices become clogged by solid particles. To determine whether or not there is a flow of gas, a short portion of the line behind the "a" valve is left bare. By feeling the temperature of this bare pipe with one's hand it is possible to detect a flow, or stoppage of flow, of gas.

If it should become necessary to flush with oil, the orifice plate should first be removed, where possible.

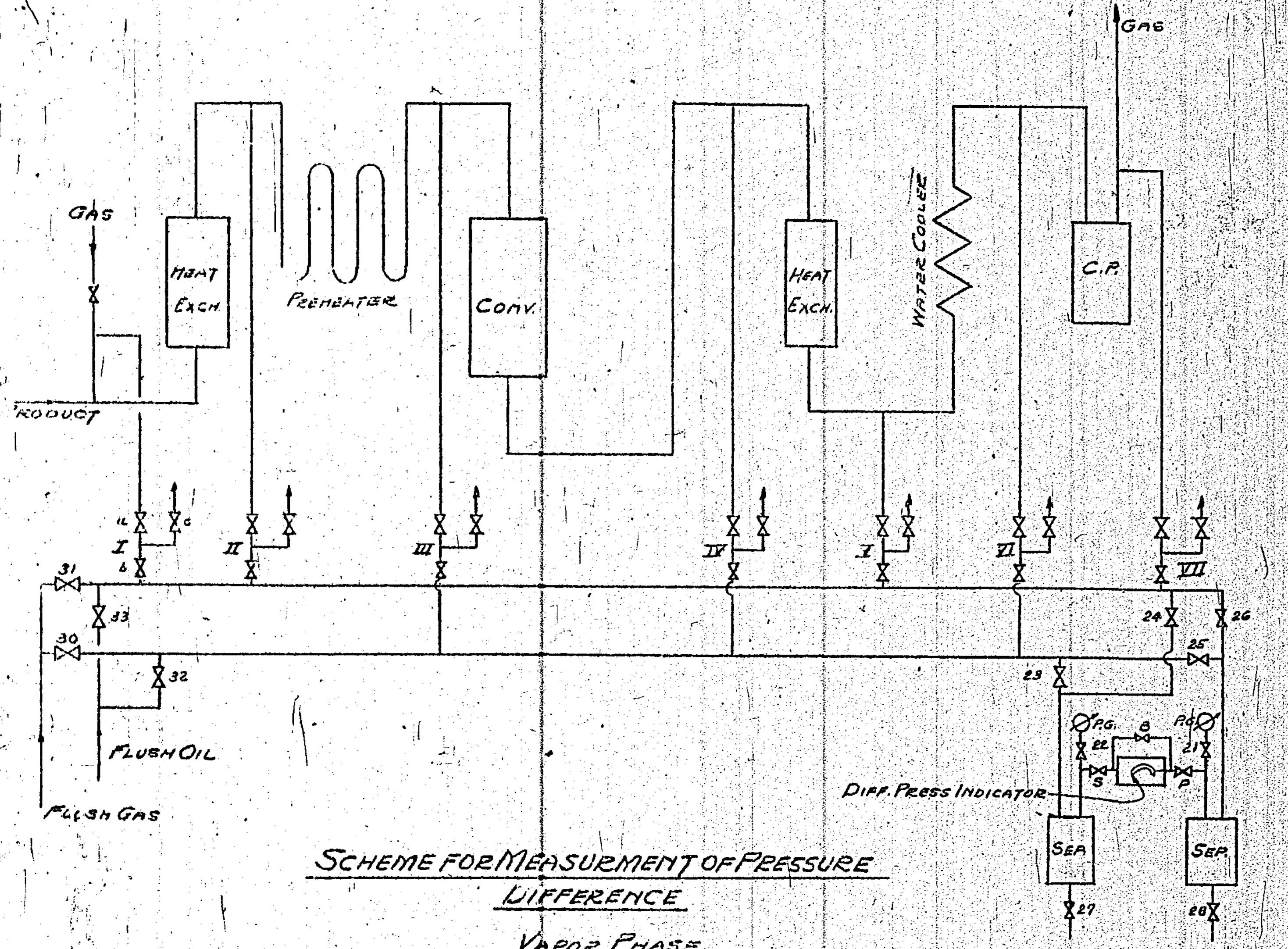
The newest stalls were also operated without orificeS and flushing gas. Assuming that the equipment is serviced satisfactorily, it will suffice, in this case, to flush the lines to the stalls in question for a short time each day with gas, in difficult cases with oil.



SCHEME FOR PRESSURE DIFFERENCE MEASURMENT, LIQUID PHASE

024

T-207



SCHEME FOR MEASURMENT OF PRESSURE DIFFERENCE

VAPOR PHASE

TOM Reel 167
Pp. 544-545

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

T-208

KCBraun
1/8/47

SULFURIC ACID WASH FOR PREHYDROGENATION MIDDLE OILS

Lu, 20 October, 1941

In the prehydrogenation of bituminous and brown coal middle oils with the newly developed prehydrogenation catalyst 8376 (7840 W 250) easily benzinated middle oils are produced @ 22 MV, though their aniline points are above the corresponding 5058 products. If it is desired to prehydrogenate weaker than with 5058, the middle oils must first be scrubbed with 50% concentrated H_2SO_4 before they can be readily benzinated with 6434. The introduction of an H_2SO_4 wash is, therefore, essential to avoid disadvantages in hydrogen consumption, anti-knock properties of the gasoline and the yield of DHD gasolines with the introduction of the new prehydrogenation catalyst. The extent of these disadvantages may be estimated in the processing of bituminous coal liquid phase gasoline and middle oil with catalyst 8376 without an H_2SO_4 wash compared to 5058:

Excess H_2 consumption	:	abt. 25 m^3/t gasoline.
Octane number reduction	:	abt. 0.5
Loss of yield in DHD process	:	abt. 1%.

117

KCBraun
1-9-47

THE INFLUENCE OF SULFUR ON CATALYTIC HIGH PRESSURE HYDROGENATION

By Donath, Lu, 27. May, 1943.

(Comment on an article by Fuchs and Brendlein in "Angewandte Chemie", 1939).

The article first describes the sulfuring of catalysts MoO_3, Fe_2O_3, MgO, and Al_2O_3 at 300° C. and atmospheric pressure with H_2S for 12 hours.

The authors found that the catalysts so treated behave differently in subsequent reductions with H_2 and steam at 430° C. The Mo catalyst gives off no sulfur, while the Fe catalyst does.

It should be remarked hereto, that none of the catalysts was sulfured to the given analyses, but still contained considerable oxygen. Judging from our experience, these catalysts can, therefore, have no activity normal to us. Obviously, no reduction in sulfur content occurs during reaction in the case of the Mo catalyst, because less sulfur is present than corresponds to the quadruple valued Mo, while the quantity of oxygen and sulfur combined approximately does. In the iron catalysts a greater sulfur content is present than corresponds to the FeS stage and this is decreased to the value corresponding to the FeS in the reduction with hydrogen. In the presence of MgO and Al_2O_3 the sulfur content even drops somewhat below the proportion of FeS.

With these catalysts, which represent no uniform sulfides, experiments were made at 200 atm. for the reduction of hexanol and the hydrogenation of benzol.

Temperatures of 434-440°C were used for the reduction of hexanol, but no thruputs are given. A reduction of 89.2% of the hexanol is obtained with Mo, one of 97.6% with the best Fe-Al catalyst, both in the presence of 3% CS_2. Without CS_2 the reduction was somewhat smaller, 83.6% and 86.2%, respectively. In these experiments the catalysts already showed deterioration after hours, which was merely delayed by the addition of sulfur in quantities up to 17% CS_2.

Compared to those results, for example, the higher alcohols of isobutyl oil are already reduced over 99.5% with a thruput of 1 at 300° C and 200 atm., when using a properly prepared molybdenum-sulfide catalyst (7846-Al_2O_3 MoS_2 NiS). An addition of sulfur has no effect and the catalyst shows no deterioration.

Fuchs and Brendlein further found that with the Fe_2O_3-Al_2O_3 catalyst in the presence of water benzol is converted about 15% into cyclohexane, even at 300 atm. Without the addition of water, but in the presence of 5% CS_2, benzol was converted into cyclohexane up to 46.5-65% at 460°C.

By comparison, we already hydrogenated benzol to 99.5% concentrated cyclohexane with catalyst 7846 W (Al_2O_3 WS_2 NiS) at 250-300 atm. hydrogen pressure and a max. 360° C., with a thruput of 0.5-1.0.

Accordingly, an addition of sulfur is not required or desired above 0.5%, at the most, when working with our sulfide catalysts. On the contrary, Varga maintains that the optimum sulfur effect is obtained with a sulfur addition of 1-15%. Based on the article discussed herein, Varga's claim may apply advantageously to improperly prepared sulfide catalysts.

In summary, Fuchs and Brendlein worked with catalysts still containing much oxygen. The activity of these catalysts is much weaker than our pure sulfide catalysts. In addition, these catalysts show deterioration even in the presence of large quantities of sulfur, while the pure, properly prepared catalysts show none.

129

028

TOM Reel 164 / U. S. Bureau of Mines / T-210
Pp. 1019-1023, / Hydro. Demon. Plant Div.

KCBraun
1-10-47

EXPERIENCES WITH PREHEATERS

Lu, 22 March, 1943.

(A brief report by D. I. Schappert on a round table discussion on the relief of liquid phase preheaters, embodied in T-83, which see. Tables and diagrams mentioned by Schappert are not available, but the diagrams in T-83 afford a helpful comparison or may even be the same. A check against the microfilm seems to indicate that Figures 3 and 4 of T-83 are duplicates of Figures 1 and 2 of T-83, respectively).

The preheater conditions in the various plants were discussed as outlined in Table I.

Three groups can be distinguished:

1. Group: Welheim and Wesseling.

Here the entire feed is run thru preheaters. About 70% of the heat input into the first converter is recovered in the heat exchangers. If the percentage of heat recovered at Leuna at 200 atm. is higher (80-90%), this is due, on the one hand, to the fact that @ 200 atm. the let-down heat exchange (double coil) provides an additional heat recovery. For 700 atm. ~~a suitable heat exchanger would first have to be provided.~~ On the other hand, the K-values of the heat exchangers at Leuna are higher (velocity).

2. Group: Scholven and Nordstern.

Bituminous coal paste causes difficulties, due to swelling, in the heat exchangers, as compared to brown coal. Due to the low cost heat in the Ruhr district, they were satisfied to confine their heat exchange to the input gas, so that only about 33% of the recoverable heat is recovered.

3. Group: Pölitz and Upper Silesia.

Here the thin paste and input gas together are passed thru heat exchangers. The thick paste is heated separately, while the remaining common heating to the reaction temperature is done in the socalled mixture section. About 30% of the heat can be exchanged by this process.

In this group, therefore, about 50% of the heat must be supplied by a gas fired preheater. This amounts to 13,000,000 kcal/h @ 70% efficiency for Upper Silesia, which is equal to almost 1.5 t oil per hour.

The high stress on the N10 material is another reason for relieving the preheater. The table shows the wall temperatures at Nordstern, Pölitz and Upper Silesia in the new and encrusted condition. While that at Nordstern is based on a crust of 8-10 mm thick, a 5 mm crust was figured for Upper Silesia. This requires a decrease in thruput of about 25%, if the circulating gas inlet temperature is not raised. Of course, it is impossible to say how long it will take to form such a crust. A check of the preheater at Upper Silesia is, therefore, urgently necessary.

Case 1 shows the preheater at Upper Silesia, as it is being installed. (Upper sketch of Figure 3, T-83, -?).

Case 2 shows the effect of the increased concentration of the thin and thick pastes. This might be possible to some extent, since the turbo-mixer has been very satisfactory at Pölitz. This will heavily burden the heat exchangers, to be sure, 52 t/h compared to 43.7 t/h. But the heat exchanger outlet temperature will drop sharply, so that more hairpin coils will be required in the mixture section, because of the smaller temperature difference, which, in turn, will cause a steep increase in the pressure difference. This procedure is, therefore, possible only in connection with a gas heat exchanger. See Case 4.

Case 3 shows the effect of the operating method with cold paste, successfully used at Nordstern. The cold paste is not taken from the preheater, as shown in the diagram, but injected directly into Converter II, or possibly heated slightly in a hairpin coils. With a somewhat higher temperature a greater injection may be possible.

Case 4 shows the favorable effect of a gas heat exchanger. A considerable saving in heat is effected. The paste inlet temperature into the heat exchanger is higher than in Case 1, 141° compared to 100° C, which may, under certain conditions, be of importance because of the viscosity. The cold paste was retained for reasons of simplicity. The gas hairpin coils are eliminated, simplifying the scheme.

<u>Case 5</u> is shown in Table 2. A "preheat converter" is installed ahead of the 4 operating converters. The preheater does not heat to 425° any more, but only to 400° C. Based on the results at Nordstern, see Table 1, it may be assumed that the converter will start reaction at a still lower temperature (390°). The preheater is now relieved due to lowering the peak temperature from 425° to 400° C. The comparison is made directly with Case 1, so that the effect of the "preheat converter" is shown <u>only</u> in the <u>lower</u> circulating gas temperature, from 600° to 540° C.

The scarcity of high pressure vessels has prevented the introduction of such a converter up to now. Nor was it formerly known at what minimum temperature Converter I would still react. Until the Nordstern operating method became known, it was believed that 425° C. was the lowest possible temperature. If it were desired to keep the circulating gas inlet temperature at 600° C., about 8 hairpin coils could be saved, so that even from the standpoint of steel requirements the introduction of a "preheat converter" is not serious, particularly since the saving in heat also equals the cost of any steel required for fuel gas production.

The other column of the table shows the case embodying all possibilities for improvements to date, such as:

1. A small increase in concentration,
2. Cold paste,
3. Gas heat exchanger,
4. Preheat converter.

In addition, some other possibilities for improvement were considered, which, of course, do not equal the effect of a preheat converter, such as:

5. Reducing the gas quantity,
6. Connecting the hot part of the preheater instead of cocurrent, for reasons of wall temperature.

Figure 5 shows a comparison between the present scheme and the scheme embodying all possibilities for improvement. The encircled figures correspond to the number of the proposed change. (See Figure 1 or 3 of T-83, -7).

Figure 6 shows the corresponding temperature diagrams. (See Figure 2 or 4 of T-83,-7). It is possible to reduce the circulating gas inlet temperature considerably and to save about 10 hairpin coils. If no attempt is made to economize on the hairpin coils, these can be further relieved.

The saving in heat equal to about 7,000,000 kcal/h @ 70% efficiency is worth noting. The stall resistance is also reduced. Only a careful test in cooperation with Upper Silesia will show which of the proposed modifications should be made.

127

031

TOM Reel 163,
Pgs. 107 to 109
and 114 to 116.

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

T-211

KCBraun
1/14/47

THE INFLUENCE OF PRESSURE AND VARIATION IN PROCESS ON HYDROGENATION

By Hupfer & v. Hartmann,
Lu, 15 October 1942.

THE INFLUENCE OF PRESSURE ON THE HYDROGENATION OF BITUMINOUS COAL.

The following table shows a comparison of conditions and results of hydrogenation of Scholven coal at 300 and 700 atm. Conversion to the higher pressures results in these advantages:

Catalysts may be used which contain no scarce metals, do not attack the converter by corrosion, and are cheaper.

A higher reaction temperature may be used, with consequent higher production, a somewhat greater decomposition, and particularly a decrease in the asphalt produced, which assures a trouble-free processing of the residue.

In spite of the higher temperature, gasification is decreased.

INFLUENCE OF PRESSURE ON HYDROGENATION

Pressure, atm.		300	700
Coal		Scholven Hydrogenation Coal	
C	%	82.7	
O	%	10.4	
S total,	%	1.0	
Available H,	%	4.5	
Alkalinity		10-11	
Catalyst		0.06% tinoxalate 1.15% NH_4Cl	1.9% $FeSO_4.7H_2O$ 1.5% Bayermass 0.3% Na_2S
Converter Temperature	%	462	480
Results:			
Decomposition	%	93	95
Thruput, $t/m^3/h$		0.18	0.27
Gasification	%	25	21
Asphalt from pure coal	%	18	11

INFLUENCE OF THE PROCESS.

The following table shows the processing conditions and the most important results of the liquifaction of Silesian bituminous coal by various processes.

From the gasoline + middle oil process to the extracting hydrogenation at approximately equal reaction temperatures the conditions change in stages with respect to:

Increase in coal thruput.

Decrease in heavy oil content of the pasting oil, which must be partly compensated by an increased let-down return.

Decrease in H_2 supply.

The extracting hydrogenation further saves the addition of Bayermass and sulfigran, with consequent better filtrable let-down.

These changes in conditions have the following effect on the results:

The thruput, the oil yield based on input coal, and the heavy constituents of the oil yield, such as asphalt, decrease. But equal boiling fractions also become heavier and H_2-poorer. While, for example, the gasoline from the gasoline + middle oil and the heavy oil processes shows an anti-knock value of less than 70 (Res), the gasoline from extracting hydrogenation has an anti-knock value of 78.5 (Res).

Gasification and, to a certain degree, decomposition decrease.

PROCESSING SILESIAN BIT. COAL @ 700 ATM.

INFLUENCE OF THE PROCESS.

Process	Gasoline + Middle Oil	30% Heavy Oil	50% Heavy Oil	Extracting Hydrogenation
Temperature, °C	476	478	480	476
Pure coal thruput, t/m³/h	0.43	0.62	0.63	0.85
Catalyst: $FeSO_4.7H_2O$, %	1.2	1.2	1.2	1.2
Bayermass, %	1.5	1.5	1.5	--
Sulfigran, %	0.3	0.3	0.3	--
Pasting Oil, proportion of Heavy Oil: Mi-Oil	100:0	85:15	73:27	0:100
Gas, m³/kg, pure coal	5.1	3.7	3.6	1.5
Processing	Centrifuging with hy oil. L.T.C. of centrifuge residue.	Centrifuging with middle & hy oil proportion 1:1 L.T.C. of centrifuge residue.	Centrifuging with middle & hy oil proportion 85:15 L.T.C. of centrifuge residue.	Filtration L.T.C. of filter residue. Topping of the filtrate.
Coal: Let-down return	1:0	1:0.20	1:0.32	1:0.50
Decomposition, %	96	95.5	96	92.8
Total thruput, t/m³/h	0.26	0.40	0.41	0.67
Oil Yield, kg/t pure coal	600	670	670	798
of which: gasol-200°, %	23	20	21	7
mi-oil-325°, %	77	45	32	14
hy oil+325°, %	--	35	47	--
bitumen, %	--	--	--	79
Gasification %	23	20	18.5	7.5
Asphalt in let-down heavy oil, %	14.7	18.0	19.3	29.0(1)

(1) Since the topping residue still contains varying quantities of middle oil, the asphalt content of the heavy oil may be somewhat higher.

TOM Reel 182 U. S. BUREAU OF MINES 035 T-212
Pp. 1123-1141 HYDRO. DEMON. PLANT. DIV.
KCBraun
1-15-47

THE INFLUENCE OF RAW MATERIAL, CATALYST AND OPERATING METHOD ON HYDROGENATION.

By Dr. M. Pier, I.G.F., Ludwigshafen, June 1938.

Besides the purely thermal processes for the production of low boiling hydro-carbons, the cracking of petroleum or the low temperature carbonization of solid fuels, formerly used exclusively, other processes have, in the course of time, become of importance, such as the polymerization of gaseous hydro-carbons from natural and cracking gases, catalytic cracking, catalytic hydro-carbon synthesis from CO-H_2-mixtures and, in particular, catalytic pressure hydrogenation. Liquid fuels can be obtained by purely thermal processes with subsequent distillation and refining only in relatively small yields from coal and other high-molecular raw materials, because of their low H_2-content, as well as from H_2-poor oils. However, the conversion of such raw materials into liquid products with only small losses is possible by splitting in the presence of a catalyst with simultaneous absorption of H_2 under high pressure.

Coal and oils were already hydrogenated under pressure by Bergius in 1913, but the process has become of practical importance only since the introduction of poison-proof catalysts by I. G. Farbenindustrie, A.G. Bituminous and brown coal, peat, coal extract, pitch, high and low temperature tars, oil shale, petroleum and its products of distillation, extraction or cracking, etc., are suitable raw materials. Valuable fuel oils, diesel oils, illuminating oils, lubricating oils, paraffins and gasolines are the refined products obtained with the highest yield. It should be especially emphasized that the steadily rising demands on the quality of the products, particularly that of the gasolines, are also being met by hydrogenation in every respect.

Suiting the process to the most varied raw materials and the desired properties of the end products is facilitated by sub-dividing it into two different working stages. In the first stage, the liquid phase, high molecular, asphalt-rich, as well as raw materials containing ash, such as coal and heavy oil residues are processed with a finely distributed catalyst, wherein, in general, only small quantities of catalyst are used for strong splitting. In the second stage, the vapor phase, hydrogenation is accomplished by passing the feed, particularly the middle and heavy oils produced in the preceding liquid phase, together with H_2, over a fixed catalyst, in vapor form or partly liquid, depending upon their boiling range and the working temperature employed.

The catalysts for processing high molecular raw materials in the liquid phase primarily effect an increased and regulated asphalt decomposition by their characteristic acceleration of the reaction. This permits an increase in thruput and the thermal auxiliary reactions and consequent gas formation are suppressed. The character of the raw materials is still perceptible in the products of the liquid phase, because the catalyst can generally be used only in small quantities.

In the hydrogenation with a fixed catalyst the course of the reaction is practically completely controlled by the catalyst, which is here used in maximum concentration. The catalyst is, consequently, much more effective than in the liquid phase. We try, therefore, to widen the range of application of fixed catalysts as much as possible. A frequent interchange is not possible for practical reasons, and a life of many months, or even years, is expected of them today. They can, therefore, be used wherever their life is not affected by the separation of high molecular, particularly asphalt-containing, substances. This is true of all oils of medium boiling range, though certain high molecular, asphalt-poor, substances may also be processed over fixed catalysts. Brown coal carbonization (L.T.C.) tar, for example, may be converted in a single stage to paraffin, lubricating or diesel oil or to a middle oil suitable for subsequent vapor phase hydrogenation.

A large number of specifically acting poison-proof catalysts are available today, in which the relation of hydrogenation to splitting effect is so adjusted that the reaction may be suited to any end product and guided in the desired direction by the simultaneous utilization of temperature and pressure influences. In the production of gasoline, for example, the manifold reaction possibilities may be utilized to obtain certain desired properties largely independent of the raw material. The products produced over fixed catalysts are well refined and stabilized. A further advantage in working with high catalyst concentrations is this, that fewer gaseous hydro-carbons, particularly methane and ethane, are formed than in the liquid phase. This is of particular importance, because much hydrogen is consumed in the formation of gaseous hydro-carbons, while the hydro-carbons themselves are less valuable than gasoline, even though they benefit the fuel market in the form of liquid gases.

The influence of temperature is of primary importance to the course of the reaction. The speed of reaction of hydrogenation and particularly of splitting increases with rising temperature. Furthermore, the equilibrium for the absorption and splitting of H_2 is constantly being displaced in the direction of dehydrogenation. At temperatures around 300° C refining takes place primarily. Thus, reactions are taking place in which no splitting of the C-C combination occurs. At a higher temperature, around 400° C, a marked splitting already occurs, depending upon the catalyst, or the product is strongly hydrogenated with hydrogenating catalysts. Thus, on the one hand, gasoline is produced with only little gas formation. On the other hand, good lubricating or illuminating oils are produced or low temperature tars containing asphalts are hydrogenated and refined. In a further rise in temperature to 450° C middle oils are obtained from high boiling oils or coal with increasing splitting. About 500° C it is possible to split without hydrogenation with suitable catalysts, or even to dehydrogenate, and produce gasolines with high aromatic content. The temperatures, at which these reaction types occur, may, of course, considerably overlap each other under the influence of catalyst and pressure.

Increased H_2 pressure generally effects increased hydrogenation. It also prevents, therefore, the separation of H_2-poor products, thus making it possible to work with higher temperatures than with a lower pressure. In the final result, the oils and gasolines produced under such conditions, may even be poorer in H_2 than with lower H_2 pressures. High pressure also results in greater reaction speeds and more raw material can, therefore, be processed in the same reaction space. As an example of the effect of pressure in the liquid phase may be mentioned the slow processing of old bituminous coal or high molecular asphalt at 200-300 atm., which, at considerably higher pressures, e.g. 700 atm. and over, is done without difficulty at satisfactory speeds. When using fixed catalysts, the range of application of the various catalysts is further increased by greater H_2 pressure. The possibility exists, for example, to obtain hydrogenation effects with greatly reduced splitting, or to obtain special effects with little hydrogenating splitting catalysts, as e.g. in the direction of anti-knock gasolines.

Besides the total pressure, the relation of oil vapor to H_2 partial pressure is also important. By increasing the oil vapor partial pressure the degree of hydrogenation is generally reduced. Furthermore, the time of passage thru the reaction space must be suited to the desired reaction.

Just as in most other hydro-carbon conversions, the reactions in catalytic pressure hydrogenation are not completed in one pass, but those constituents not completely converted to the end product are either recycled or processed in a separate reaction. For example, in the liquid phase hydrogenation of coal the heavy oil produced is recycled, if we desire to produce middle oil with little liquid phase gasoline. If the middle oil is recycled and the heavy oil formed is withdrawn from the process, the coal yields only heavy oil and liquid phase gasoline. Even though a raw product can be completely converted into gasoline in the liquid phase by a recycling all the middle oil, this is never done, because a far greater gasification takes place than if the middle oil is converted into gasoline over a fixed catalyst.

In the vapor phase, also, the middle oil is generally not converted more than 50-80% in one pass and the unconverted middle oil is separated from the gasoline by distillation and recycled. In this manner a higher gasoline yield is obtained by a better utilization of the reaction space. Besides, the boiling curve of the gasoline may be controlled at will.

Figure 1 shows diagramatically the course of a number of pressure hydrogenation reactions as I have described them. It may be observed how much the character of the liquid phase product is dependent upon the raw material and how easily it may be changed in the vapor phase with fixed catalyst.

Liquid Phase Hydrogenation.

In the production of gasoline it is the task of the liquid phase to produce intermediate products from high molecular raw materials. These cover the whole boiling range of gaseous hydro-carbons to the heaviest oils more or less uniformly. Their properties resemble those of the distillation or low temperature carbonization products of the corresponding raw materials.

If, for example, distillation residues boiling above 325° C from an asphaltic base and a mixed base crude oil are processed in the liquid phase, middle oils well suited for diesel fuel are produced, whose properties closely correspond to those of the distillation middle oils from the original crude oil, as shown in Table 1.

Table 1

Distillation and Liquid Phase Middle Oils from Various Crude Oils.

Middle Oil 180-325°C	Spec. Grav. @ 15° C	Aniline Point °C	Aniline Point of the Fractions		
			210-230°	240-270°	280-310°
From mixed base crude oil:					
Distillat. middle oil --	0.840	61	56	59	66
Liq. Ph. " " --	0.838	57	52	56	61
From asphalt base crude oil:					
Distillat. middle oil --	0.856	50	47	50	54
Liq. Ph. " "	0.851	51	49	52	54

It may be noticed that the hydrogen contents indicated by the aniline point of the corresponding fractions of the liquid phase and distillation products are very much alike. This rule, indicated here in two examples, is so generally valid that the properties of hydrogenation middle oils from a crude oil residue may be predicted with great precision, if the properties of the middle oil contained in the original crude oil are known.

There is a similar, though not quite so close, relation between the coals, if the hydrogenation middle oils from coal are compared with the corresponding middle oils from L.T.C. (low temp. carbonization) tar, after the phenols have been removed from both. See Table 2.

Table 2

Tar Middle Oils and Liquid Phase Middle Oils from Coal.

	Total Middle Oil 180-325° C	Dephenolized Middle Oil (180-325°C)			
		Spec. Grav./ 15° C of Fractions		Aniline Point, °C of Fractions	
	% Phenols	240--270°	280-310°	240-270°	280-310°
From brown coal:					
L.T.C. tar middle Oil	24	0.899	0.912	15	31
Liq. Ph. " "	14	0.878	0.906	24	33
From Bitum. Coal:					
Crude tar middle oil	27	0.940	0.980	-6	-10
Liq. Ph. " "	9	0.938	0.972	-15	-14

It may be observed that the coincidence in the hydrogen values is not as complete as with petroleum products, which is due, among other causes, to the fact that the heavy oils represent only a relatively small proportion of the original coal, while in hydrogenation practically the entire coal appears as oil. The phenol content of the crude middle oils is larger in low temperature carbonization than in liquid phase hydrogenation. However, the absolute yield in phenols, based on the coal, is larger in hydrogenation.

The yield in paraffin, also, is considerably greater in the direct hydrogenation of brown coal than the quantity of paraffin which may be recovered from the L.T.C. tar in the low temperature carbonization of the same quantity of brown coal.

In the production of gasolines from heavy oils or from coal the middle oils are the principal product of liquid phase hydrogenation, plus about 20% gasoline. In this gasoline the character of the raw material may still be recognized, as shown in the example of some liquid phase gasolines from petroleum in Table 3.

Table 3

Liquid Phase Gasolines from Various Crude Oils.

Liq. Ph. Gasoline From:	Residue from mixed base petroleum	Residue from asphalt base petroleum	Cracking residue from asphalt base gas oil
Spec. Gravity	0.719	0.731	0.788
% to 100° C	36.5	26.1	13.0
% to 170° C	90.5	88.7	82.0
Aniline Point of Fractions:			
80-100° C	53	56	37
100-140° C	52	53	25
150-180° C	53	52	11
190-210° C	--	--	7
Octane number, (research method)	53	57	73

The octane number of liquid phase gasoline rises from the ~~mixed base to the asphalt base crude oil to the aromatic cracking~~ residue, which yields a liquid phase gasoline with an octane number of 73. The aniline points of the fractions indicate that the drop in the aniline point with rising boiling point is greater in the products richer in aromatics than in those richer in hydrogen. The gasoline from the easily splitting mixed base crude oil is rich in constituents boiling below 100° C., while the oils poorer in hydrogen yield gasoline with a lower content of low boiling constituents.

An example of the properties of chemically refined liquid phase gasolines from coal is given in Table 4.

Liquid Phase Gasolines from Various Coals.

Liquid Phase Gasoline From:	Brown Coal			Bitum. Coal	
	Young				
	Rich in bitumen	Poor in bitumen	Old	Gas flame coal	Fatty Coal
% Phenols in raw Gasoline.	6.0	5.0	5.5	6.3	2.8
Refined Gasoline:					
Spec. Grav.	0.738	0.758	0.739	0.734	0.737
% to 100° C.	36	38	49	47	43
Composition:					
% paraffin	50	37	40	38	28
% naphthene	28	39	44	45	54
% aromatics	18	13	12	14	16
% unsaturated	4	11	5	3	2
Octane number. (research method)	62	67	69	69	70

The octane number of liquid phase gasolines from coal is higher than that from crude oil and from coals rich in bitumen nearly equal the values obtained in processing aromatic gas oil residues. As expected, fatty coal yields a gasoline poorer in hydrogen than that from the gas flame coal richer in hydrogen coming from the same field. Very generally speaking the liquid phase gasolines from coal contain much low boiling constituents because they are produced by heavy splitting.

With raw materials relatively rich in hydrogen the anti-knock values of the liquid phase gasolines drop in the higher fractions, but not as much as in natural gasolines or purely paraffinic gasolines. In gasolines from gas oil residues poor in hydrogen the anti-knock values of fractions above about 130° C rise again. The rise in bituminous coal gasolines is even sharper, which is related to the high aromatic content of the higher fractions. It is, therefore, proper to cut off liquid phase gasolines from aromatic raw materials as high as possible; those, from raw materials rich in hydrogen should be cut off lower. Liquid phase gasolines from aromatic raw materials are still further improved, if refining is effected with catalysts under hydrogenating conditions instead of with the usual refining media, whereby phenols, possibly present together with hydrogen under pressure, are reduced to aromatic hydro-carbons.

Hydrogenation With Fixed Catalyst.

Hydrogenation with fixed catalyst has found such wide spread application because the reaction may almost be influenced at will by the kind of catalyst, the temperature and pressure. On the one hand, it is possible to work with strong splitting up, on the other hand to obtain a more or less strong hydrogenation without splitting the carbon structure.

An important application of pressure hydrogenation taking place without splitting is the refining of gasolines and benzol, as they are produced in cracking, low temperature carbonization, coking, or liquid phase hydrogenation.

Raw benzol from bituminous coal coking is catalytically converted into a stable product, hardly richer in hydrogen, at a pressure as low as about 40 atm. More motor benzol can be produced by hydrogenation, not only because the losses formerly incurred in benzol refining are practically eliminated, but also because the middle and heavy benzol boiling above the motor benzol can also be used. These fractions, which hardly yield motor fuels with sulfuric acid, are completely saturated at about 50-200 atm. by careful hydrogenation without an appreciable loss in octane number. Table 5, for example, shows in the iodine number of a middle benzol fraction, boiling between 140-180° C, how far saturation goes. At the same time only an imperceptible hydrogenation of aromatics takes place, as indicated by the spec. gravity and the octane number. Furthermore, the color becomes as clear as water and the product is freed of sulfur to 0.006%.

In the same way, L.T.C. gasolines from bituminous and brown coal are refined, which, at 200 atm, yield stable gasolines, as clear as water and almost free of sulfur.

Table 5.

Hydrogenation of Middle Benzol.

Middle Benzol	Raw	Hydrogenated
Spec. Gravity	0.833	0.865
Start of boiling, °C	136	134
50% point, °C	155	154
95% point, °C	178	179
Color	Straw yellow	Clear as water
Iodine number	61	4.5
% Sulfur	0.18	0.006
Octane number (motor method)	Abt. 100	Abt. 100

Table 6 shows an example of the refining of liquid phase products, a liquid phase gasoline from a young bituminous coal with a boiling end point of 215° C.

Table 6.

Hydrogenation of Bituminous Coal Liquid Phase Gasoline

Bituminous coal liquid phase gasoline	Chemically refined	Refined by pressure hydrogenation	
		a	b
Spec. Gravity	0.794	0.790	0.785
% to 100° C	33	35	43
% to 170° C	75	78	80
End point, °C	215	212	220
% Paraffin	28	29	28
% Naphthene	36	38	18
% Aromatics	32.5	31.5	52.5
% unsaturated	3.5	1.5	1.5
Octane number:			
Research method	72	71	85
Motor "	66	67	77

This gasoline suffers considerable loss in refining with lye and sulfuric acid, due to olefin and phenol contents, and so yields a motor fuel with an octane number of 72 by the research method and with an aromatic content of 32%. By means of pressure refining and a satisfactorily hydrogenating catalyst a gasoline is obtained without loss @ 200 atm. and 300° C, which about equals the chemically refined in octane number and aromatic content. By using special catalysts and dehydrogenating conditions in the presence of hydrogen a considerable improvement of the motor characteristics of the gasoline may even be obtained in one refining pass. It will then have an octane number of 85 (research-method) and contain over 50% aromatics.

The phenols in the raw gasoline from coal must be removed in chemical refining, which greatly reduces the gasoline yield. In pressure refining they are converted into hydro-carbons and remain as such in the gasoline. Depending upon the hydrogenation conditions applied, they form aromatics or naphthenes without loss by splitting of hydro-carbons.

The pressure refined gasolines are colorless, odorless and lightproof and in tests and boiling characteristics correspond to the best commercial gasolines. The content of unsaturated equals 1-1.5%, the gum content far below 10 mg/100 cm^3 and the sulfur content below 0.01%.

The most important field of application of the vapor phase is splitting hydrogenation of middle oils to gasoline. Just as in the liquid phase, the raw materials are important for the properties of the gasoline. However, the determining factors are the catalyst and the processing conditions.

The dependence on the chemical structure of the raw material is particularly noticeable in the motor behavior of the gasolines. Table 7 shows the specific gravity and octane number of several gasolines produced under comparable conditions from various raw materials. The octane number of the gasolines rises with decreasing hydrogen content of the middle oils. For auto gasoline from H_2-poor raw materials, such as brown coal, asphalt base crude oils, cracking residues and bituminous coal it equals about 67-75. If gasolines with lower end point are produced the octane numbers rise. Very H_2-poor aromatic middle oils may also be obtained from H_2-rich middle oils by solvent extraction. One way to obtain good gasolines with high yield from very H_2-rich middle oils, such as are produced by the CO-H_2 synthesis, is to dehydrogenate them together with H_2-poor middle oils.

Table 7

Auto Gasoline from Various Raw Materials.

Middle Oil Feed from:	Auto Gasoline	
	Spec. Grav.	Octane No. (Motor Method)
Paraffin	0.680	45
Crude oil, mixed base	0.722	64
Crude oil, asphalt base	0.728	67
Shale oil, paraffinic	0.712	65
Shale oil, asphaltic	0.732	66
Brown coal L.T.C. tar	0.734	65
Brown coal liquifaction	0.735	66
Crude oil cracking residue	0.745	74
Bitum. coal liquifaction & extract	0.745	74
Bitum. coal high temp. tar	0.748	75

How much the quality of the gasoline from the same raw material may be influenced by the catalyst and processing conditions is shown in Table 8. Several groups of catalysts are available today. The first and most important group includes catalysts "A", which hydrogenate and split strongly and may be used for all feeds in the vapor phase. Gasolines produced by them show octane numbers about equal to distillation or L.T.C. gasolines from the same raw materials. Column "A" of Table 8 shows a gasoline so produced from bituminous coal middle oil.

Table 8

Auto Gasoline from Bitum. Coal Middle Oil with Various Catalysts.

Catalyst	A	B	C	D
Spec. Gravity	0.735	0.745	0.770	0.830
Octane Number:				
Research Method	67	75	78	95
Motor Method	66.5	74	75	83

Much better octane numbers at equally high gasoline yield are obtained with catalysts of a second group, which hydrogenate weaker with strong splitting. Corresponding gasolines are shown in columns "B" and "C" of Table 8. These catalysts develop their full splitting effect with almost all petroleum middle oils. With oils containing oxygen and nitrogen, such as from coals or tars, a preparatory treatment is required by chemical refining or with a hydrogenating catalyst in a socalled prehydrogenation stage. In some cases the use of higher pressure, e.g. 600 atm. and over, is advisable. The processing of impure materials then also becomes possible. Furthermore, it becomes possible to work with weakly hydrogenating catalysts of this group.

All hydrogenation gasolines produced by these two groups of catalysts have a relatively high naphthene and isoparaffin content and are characterised by a good lead sensitivity of their octane number.

A third group of catalysts "D" enables the production of H_2-poor gasolines especially rich in aromatics. Higher temperatures, around 500° C, are then used. The yield in auto gasoline, which equals 90%/wt. with the operating methods here before mentioned, is here below 90%/wt. It becomes smaller, if we aim at a greater aromatic content of the gasolines and the middle oil used is paraffinic. Column "D", Table 8, shows such a gasoline obtained from bituminous coal middle oil which contains 50% aromatics at an octane number of 95 (research method).

Table 9.

Auto Gasoline from Mixed Base Petroleum Middle Oil with Various Catalysts.

Catalyst	A	B	C	D
Spec. Gravity	0.716	0.722	0.730	0.787
Octane Number:				
Research Method	57	64	72	80
Motor Method	58	64	70	74

In the benzination of a mixed base petroleum middle oil, as shown in Table 9, the gasolines obtained with the described catalyst groups also differ in a similar manner. By using the catalyst of group "D" a gasoline with an octane number of 80 (research method) can be produced, which contains over 30% aromatics. Hydrogen poor middle oils from petroleum, e.g. cracked or asphalt base middle oils, yield still higher octane numbers. The differences in the gasolines produced by different catalysts are also illustrated in the aniline point curves of the gasoline and middle oil fractions in Figure 2. The decreasing hydrogen content from "A" to "C" is clearly recognized.

Table 10

Auto Gasoline from Brown Coal Tar Middle Oil Produced by Various Methods.

Production of Middle Oil	With finely distributed catalyst	With fixed catalyst
Auto Gasoline:		
Spec. Gravity	0.734	0.730
Octane Number (Motor Method)	65	69

The method of producing or preparing a middle oil also influences the quality of the gasoline. Table 10 shows two gasolines from brown coal tar. The middle oil feed in the first column was obtained by splitting liquid phase hydrogenation from brown coal L.T.C. tar, that in the second column by careful, little splitting hydrogenation of the tar with a fixed catalyst. Here the paraffin in the tar was not split to middle oil, but was separated first as such. With approximately equal boiling curve, specific gravity and aromatic content the second gasoline has an appreciably higher octane number.

Table 11.

Hydrogenation Aviation Gasolines from Petroleum Middle Oils.

Hydrog. Gasoline from:	Mixed Base Petrol. Middle Oil	Asphalt Base Petrol. Middle Oil
Spec. Gravity	0.718	0.725
% to 100° C	57	72
End point, °C.	145	135
Vapor Press. (Reid 38°)	0.48	0.49
Octane Number (Mot. Meth.)	72	77
O.N.-M.M. + 0.09%/Vol. tetraethyllead	90	91.5
O.N.-M.M. + 0.27%/Vol tetraethyllead.	98	100

Hydrogenation gasolines are excellently suitable for aviation engines because of their high stability, good anti-knock qualities and lead sensitivity. The properties of two such gasolines obtained from petroleum middle oils are given in Table 11.

This table shows the high octane numbers of aviation gasolines produced by hydrogenation and particularly their high lead sensitivity. The gasoline from an asphalt base oil has an octane number of 77 (motor method), which is increased to 91.5 by the addition of 0.09%/vol. of tetraethyllead and to 100 by 0.27%/vol. As shown in Figure 3, the lead sensitivity of hydrogenation gasolines not mixed with tetraethyllead is still very good, inspite of their high anti-knock value (Klopfwert), and with the same basic octane number it is better than in distillation gasolines from petroleum.

Industrial Application of Hydrogenation.

Certain advances in the field of chemistry and physical chemistry of catalytic hydrogenation have been shown in characteristic examples. Besides, it is of the utmost importance to the industrial application of the process that the high pressure equipment field has kept pace with this development. The extent of the problem to be solved in common with the steel industry may be gathered from the fact that material containing sulfur can be safely processed with hydrogen today in reaction converters of more than 10 m^3 capacity at 500° C and 700 atm. pressure.

In the Ammoniakwerke Merseburg the "Leuna-Benzin" has been produced since 1927. By far the greatest part of it comes from Central German brown coal. Other available raw materials, such as brown coal L.T.C. tar, bitum. coal tar oils and German crude oil are, at times, processed to gasoline. Other hydrogenation plants in Central Germany also process local brown coal, though this is not directly hydrogenated but is first carbonized (L.T.C.) and the tar then hydrogenated to gasoline, because the major product of carbonization, the L.T.C. coke, can be profitably utilized by central power plants.

Bituminous coal has also been successfully hydrogenated on an industrial scale in Germany since 1936. Besides the direct hydrogenation of bituminous coal to gasoline the field of bituminous coal extraction with subsequent hydrogenation of the tar pitch therefrom has been explored. In other countries, too, the process is applied industrially, such as the processing of oil in the U.S.A., bituminous coal hydrogenation in England, and iso-octane production in various other countries. Two plants are being built in Italy for the production of high grade gasolines and lubricating oils from asphalt base crude oil. Other raw materials can also be processed there.

The process has been successfully applied in industry. The newer plants have reached their nominal capacity in a comparatively short time.

It is also especially important that all the raw materials in question, coal, peat, tars, shale oil, petroleum, and their constituents, can be equally well processed in a hydrogenation plant. A plant may be switched from one raw material to another, or use either domestic or foreign raw materials as conditions may dictate. The core of the plant, the high pressure section, is not essentially changed thereby, though the equipment for raw material preparation and processing of the product must be suited to them.

Just as the raw materials, the finished products may also be chosen with the greatest selectivity in catalytic hydrogenation. Instead of, or besides, high grade gasoline diesel oil or fuel oil can also be produced in varying volume proportions, as well as lubricating oils and paraffins from suitable raw materials.

The capacity and variety of catalytic pressure hydrogenation and its successful application have had this effect, that the process will be by far the most important factor in the future German supply of motor fuels and mineral oils. The importance already gained by this process may be gauged by the fact that in 1937 Germany produced almost twice as much gasoline by catalytic pressure hydrogenation, 800,000-900,000 tons, as its entire benzol production.

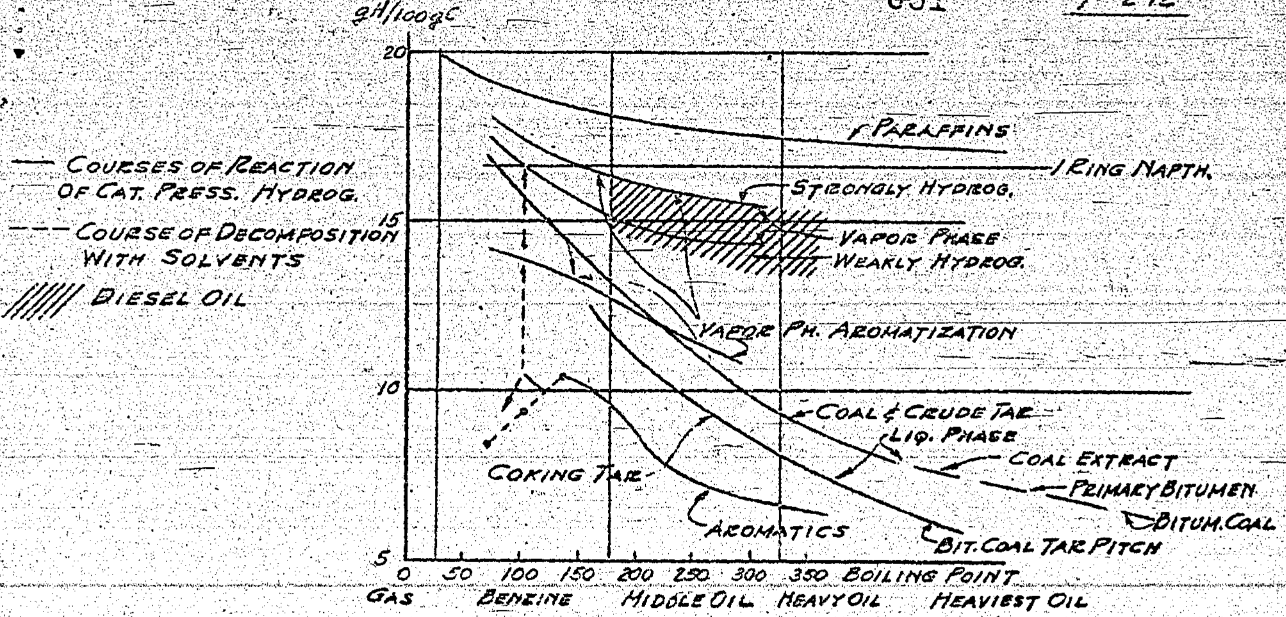


FIG. 1 HYDROGENATION OF BITUMINOUS COAL, LIQUID & VAPOR PHASE

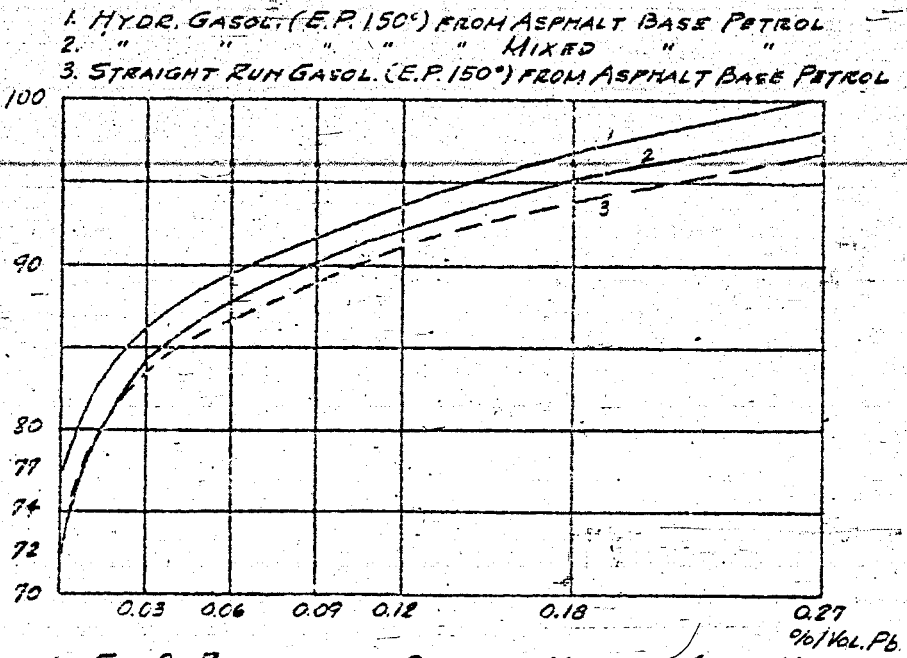
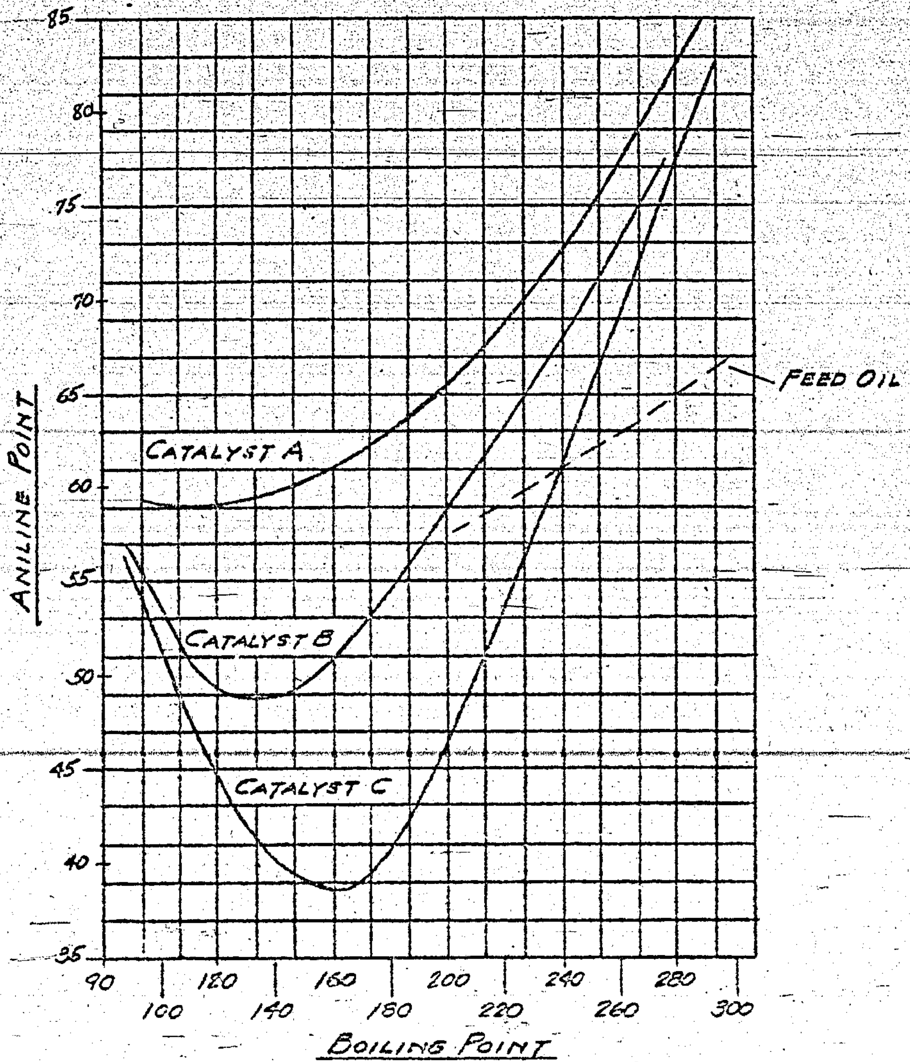


FIG. 3 RAISING THE OCTANE NUMBER (C.F.R. MOTOR METHOD) BY TETRAETHYL LEAD ADDITION.



ANILINE POINT IN RELATION
TO BOILING POINT

FIG. 2

BENZINATION OF MIXED BASE
PETROLEUM MIDDLE OILS

U. S. BUREAU OF MINES T-213
HYDRO. DEMON. PLANT DIV.

Torrance, California
January 14, 1947

Dr. Frese's Report on the Measurements of Temperatures in High Pressure Stalls.

1). Supervision of temperatures.

The optimum reaction results of a high pressure hydrogenation stall depend on a definite temperature of reaction, which differs depending on the nature of the feed and the method of operation (liquid or vapor phase). The greatest accuracy in maintaining such required reaction temperatures is obtained by having a very elaborate arrangement of temperature measuring stations over the whole unit (v. accompanying sketches). The temperatures are constantly supervised by an operator, who sets them to the required level by certain manipulations, such as changing amount of cooling gas, regulation of preheater temperatures etc. Some of the temperature measuring stations serve the additional purpose of determining the heat transfer values of the different units of the installation or for the study of the reaction mechanism.

For this purpose, all the thermocouples are connected to a cold junction box, kept at a constant temperature, and to a common instrument panel, there thermocouples conveniently connected with an alarm system which will announce any disturbances. The cold junction has been kept at 20° in Germany by means of water heated with steam, later at 30°. Within the last years an electrically heated block of copper was used, maintained at 40°. This arrangement has been found more convenient. When the temperature of the cold junction rises, the danger from the operator not immediately recognizing the rise in the converter temperature is greater, than when the temperature drops. Drop in temperature of the cold junction will manifest itself in a reduced yield because of the drop in the converter temperature.

The operator at the control board controls the converter temperature by a continuous supervision of all the couples, and maintains it at a proper level by proper measures (varying the amount of cold gas, regulation of fuel gas in the preheater). The principal converter thermocouples will naturally be more frequently plugged in, than the less important shell or cover couples. Similarly, he records on a operation log sheet the more important readings every quarter of an hour, the less important ones every half hour, and the unimportant ones every 2 to 4 hours. To have proper replacement at least 2 converter operators should be present on each shift, and they alternate in the reading of the temperatures and its recording. This function of the operator must be considered as being very important and responsible, and requires a certain amount of resourcefulness and responsibility. This is developed in the course of time.

An other duty of the operator is to observe continuously all the recording and alarm instruments, and to act on the strength of the information furnished by them. The most important data on the operation of stall are entered regularly into the converter log.

The German log book appeared about as follows:

time. atm. Temperatures	cold junct.	gas		cold gas	inj. li.
		inlet	outlet		

HOLD li.	Catchpot		water inject.	gravity recorder	Stall pressure differ. atm.	heat. gas		Remarks
	li	sp.gr.				mm	m³	

The most important information for the supervision of the process, such as solids, ash in the feed, ash in the HOLD, etc., are entered in proper places.

Arrangement of the thermocouples.

Depending on construction, three kinds of measuring arrangements are in use:

1) thermocouples in protecting tubes

2) thermocouples welded on

3) thermocouples in drilled holes

The first kind mentioned, originally the most widely used was obtained by placing the thermocouples in protecting tubes, in most cases introduced into tee pieces in the pipe line by means of gasket connections. It has however been found, that these protecting tubes in pipe lines carrying solids became eroded, and this might lead after some time to grave disturbances. It was next tried to replace these protecting tubes with welded-on thermocouples (the welds insulated). This method of measuring temperatures has been found very satisfactory, and later, for reasons of economy, this method was also used in pipe lines where no solids were present. Naturally, teperature measurements obtained in this way are not absolutely correct. Nor was it really a question of measuring accurately the temperatures at these points, and it was sufficient to record rapidly and accurately the relative variations, and these were so recorded.

In the converter proper, thermocouples installed in protecting tubes could not be dispensed with. At first these pressure resistant protector tubes were closed on the outside to withstand a low pressure only. It has however been found in the first hydrogenation installation in Leuna, that these protecting tubes were worn through inside the converter, and that the pressure in the stalls was released through these tubes and fires would be caused. After one such fire a sticky asphalt deposit covered all pipe lines and space at a distance of several 100 meters from the place of the mishap. It had then been decided to prevent this kind of damage by a pressure-tight closure of the tops of the protecting tubes. The thermocouple wires were drawn through the connections as in spark plugs, while a pipe line on the side led to a manometer, the pressure of which was checked daily. Several protecting tubes may be connected to a single manometer, and measured separately. When there is pressure in a previously evacuated pipe line, this pipe line must be disconnected and the stall eventually shut down for the replacement of the protecting tube.

When stall operations are started, all the protecting tubes are first evacuated by the use of vacuum pumps or water suction pumps (occasionally also repeatedly filled with nitrogen) in order to eliminate traces of moisture, which may occasionally produce entirely false reading through the production of additional thermal currents*.

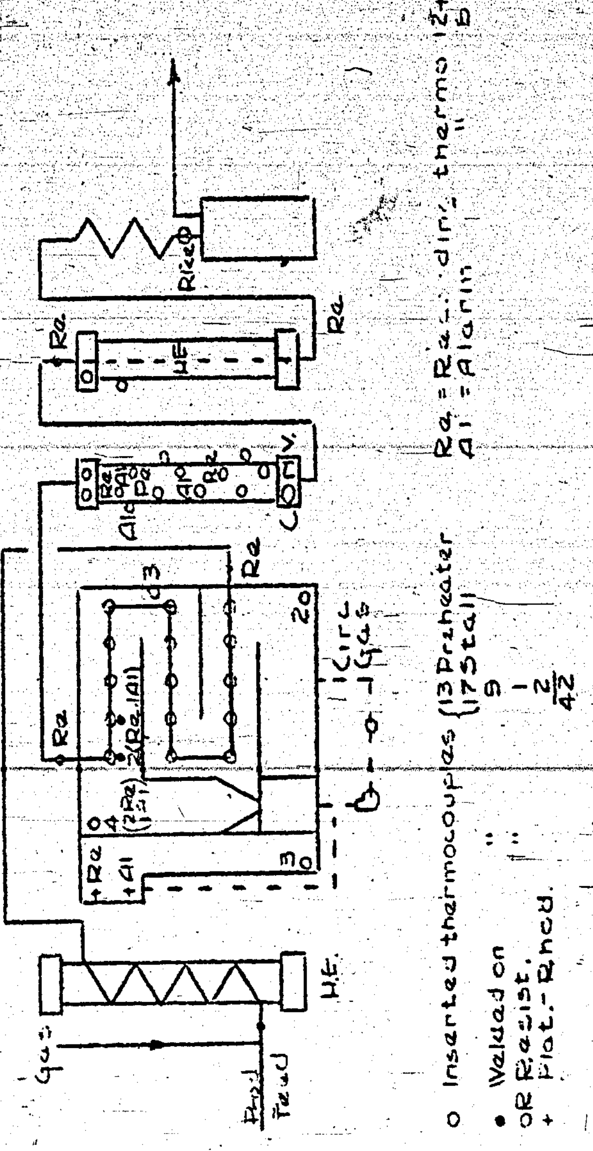
A few thermocouples are used for the measurement of the outer wall temperatures of the hairpin tubes in the hottest part of the preheaters. They are set at different levels of the tubes by welding them to the tubes, and the welds are not insolated.

In addition, some of the more important thermocouples are connected to recording instruments on the instrument board. (They are marked Re on the sketch). They serve as a check on the proper functioning of the operator and furnish the basis for the evaluation of disturbances as well as for the recognition of disturbances (exchanger shorts, solid content of the HOLD, and the like).

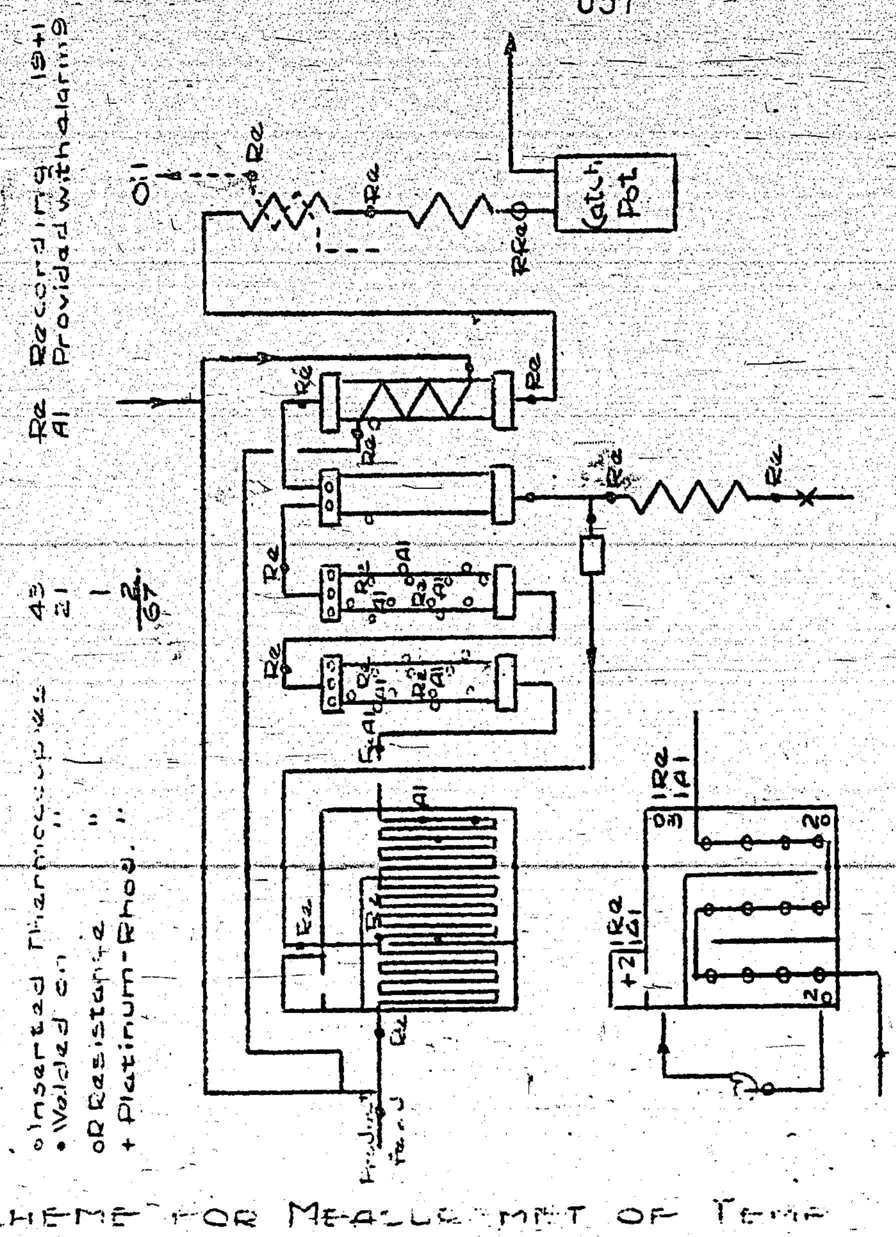
Some of the thermocouples are provided with alarm signals, (chiefly converter thermocouples). They are intended to call the operators' attention to the necessity of taking proper precautions at the moment of appearance of danger.

* The temperature of the converter shell and covers is measured by thermocouples inserted into drilled holes drilled at the critical points.

W. M. STERNBERG



SCHEME FOR MEASUREMENT OF TEMPERATURE
(VAPOR PHASE)



SCHEME FOR MEASUREMENT OF TEMP
LIQUID PHASE

TOM Reel 182 U. S. Bureau of Mines 058 T-214
Pp. 1089-1112 Hydro. Demon. Plant Div.
KCBraun
1-20-47

PROBLEMS OF INDUSTRIAL HYDROGENATION

By Dr. Carl Bosch, Chairman of the Board
of Directors, I.G. Farbenindustrie, A.G.,
Ludwigshafen/Rh.

A lecture before the Norwegian Academy of Sciences, Olso, 6 October 1933. (Abridged).

Hydrogenation has gained steadily increasing importance in the chemical industry in the past decades. Around the turn of the century it was still generally understood to be the absorption of hydrogen by unsaturated organic compounds. Today we know that the term hydrogenation has a much broader meaning. An unsuspectedly large number of syntheses of organic and inorganic chemistry are based on the absorption of hydrogen by elements, radicals or compounds capable of absorbing it. However, I should like to cinfine myself to the three important industrial processes of:

Hydrogenation of nitrogen to ammonia,
Hydrogenation of CO to methanol and higher alcohols, and
Hydrogenation of coal, petroleum and tar to gasoline,

which have been developed by I.G. in the past decades.

Today, I should like to speak of the problems encountered in the broadening and continued development of the hydrogenation processes. Although three of the processes have several points in common, the difference in reactions offers a multitude of new problems of great importance. All three of them use the same raw materials, air, steam, and coal or coke. From these raw materials, hydrogen is produced for all three of these processes, which is conducted into the further reaction process with nitrogen for the ammonia synthesis, with CO for the methanol synthesis, and by itself for the hydrogenation of coal. The gases are cleaned for all three of these syntheses, though the gas cleaning differs in the various processes, because each process requires a different degree of cleanliness of H_2 or the mixed gases. The cleaned gases are compressed and so added to the catalytic processes proper, which differ in various ways, due to the variation in the chemical reactions.

Table 1 gives a deeper insight into the mechanism of the reactions. I have indicated the chemical equations of the various syntheses and have shown with them the most important physical and chemical data. The ammonia and methanol syntheses can be represented by unequivocal equations, but the process of coal and oil hydrogenation can not be formulated so definitely. This process consists of numerous individual reactions taking place at the same time, which may be essentially combined into two main groups. In the hydrogenation of coal the object is, on the one hand, to convert the carbon present in high molecular but H_2-poor combinations into hydro-carbons by hydrogenation, on the other hand, high molecular hydro-carbons must be converted into gasolines by splitting hydrogenation.

The first side column shows the consumption of hydrogen per ton of product to be produced. All three processes require an extraordinarily large, though varying, amount of hydrogen, and the figures indicate that the method of hydrogen production plays an important role for them.

Table 1

Reaction Formula of Hydrogenation Processes.

	Reactions	m^3 H_2/t Product	Heat of Reaction cal/mol
Ammonia synthesis	$N_2 + 3 H_2 = 2 NH_3$	2000	+12
Methanol "	$CO + 2 H_2 = CH_3 OH$	1400	+21
Hydrogenation of:			
Coal	Coal + H_2 = Gasoline	abt 2500	exotherm
Petroleum	Petrol + H_2 = "	" 750	"
Tar	Tar + H_2 = "	" 1000	"
	Side Reactions		
Methanol synthesis:			
Isobutylalcohol	$4 CO + 8 H_2 = C_4H_9OH + 3H_2O$	2420	+33
Methane formation	$CO + 3 H_2 = CH_4 + H_2O$	4200	+52
Hydrogenation of coal, petro, & tar:			
Methane formation	$C_{16}H_{34} + 15H_2 = 16CH_4$	1300	+197
	$C_6H_5 . CH_2 . C_6H_5 + 20H_2 = 13CH_4$	2150	+273

The last column shows the heat of reaction of the processes. All three processes are exotherm, though with appreciable differences here also. Basically, the law of exotherm reactions must be considered valid for all three syntheses, according to which the equilibrium is displaced in favor of conversion with decreasing temperature, while the speed of reaction increases with rising temperature. An important task will, therefore, be to find the most favorable temperature conditions for the reactions and to construct the reaction space so that the optimum temperature may be constantly maintained by proper withdrawal of the heat developed. One thing further may be taken from the table. The chemical formula for the first two reactions indicate that volume contractions take place in the conversions. The same thing may also be said of certain partial reactions of hydrogenation. This makes it appear advantageous to work with higher pressures.

Another important task, not directly derived from the table, is the speeding up of the reactions. Most hydrogenation processes proceed very sluggishly and such reaction speeds as must be assumed for industrial applications can only be obtained with the use of catalysts. In most processes, however, catalysts have further tasks. I should like to point to the other part of the table, which shows that numerous side reactions are possible between the materials involved in the reactions in the methanol synthesis and particularly the production of gasoline by hydrogenation. These conversions are, generally speaking, entirely possible under the thermodynamic conditions of the processes, and the task of the catalyst is also to eliminate the side reactions as far as possible and to direct the conversion so that the desired product may be obtained with the highest possible yield.

I believe I have outlined the main problems, without whose solution the industrial application of these hydrogenation processes would be impossible. The production of hydrogen, the suitable construction of the reaction spaces and the utility and durability of the catalysts, as well as of the materials, must be solved technically and economically.

I should now like to go into the solution of these problems more in detail, first of all, the production of hydrogen. Various possibilities exist for the industrial production of hydrogen. Their choice depends upon the available raw materials and source of power. Other factors, however, are of the utmost importance for our syntheses. For example, a mixture of hydrogen and nitrogen is required for the production of ammonia. The admixture of gaseous hydro-carbons is undesirable because they become concentrated in the recycling process of the syntheses and must be removed from the circulating gases by decompression, in which process hydrogen losses are unavoidable.

A mixture of H_2 and CO must be produced for the methanol synthesis. The admixture of nitrogen and hydro-carbons cause undesirable concentrations in the circulating system.

Pure hydrogen is required for the gasoline synthesis. Nitrogen and hydro-carbons are just as undesirable here as in the methanol synthesis.

Of all industrial hydrogen processes, electrolysis is the simplest, because it produces a pure gas from the start. If this process is used for the ammonia synthesis, nitrogen must be produced separately, either by the liquifaction of air or by burning hydrogen in air. Hydrogen electrolysis is less suitable for the methanol synthesis, since recourse would have to be had to coal for the CO required. Because of the current requirements, electrolysis can unfortunately be used industrially only where cheap water power is available, such as here in Norway or in Upper Italy.

With the development of the ammonia synthesis we also developed the production of hydrogen from coke water gas. This process is at present well suited for the manufacture of ammonia, if cheap coke is available. The intermittent hydrogen process has this defect for the methanol and gasoline syntheses, that bubble gases containing nitrogen are obtained with the water gas by the periodic change. If the nitrogen content is to be held within tolerable limits, the water gas produced at the start of each gasification must be collected by itself and only about 75% of the total production can be used for hydrogenation. A solution of this difficulty has long been seen in the continuous gasification of oxygen and steam mixtures. Fränkl-Linde recently succeeded in improving the oxygen equipment so that oxygen can be produced industrially at reasonable cost.

The production of hydrogen from brown coal represents a problem of the greatest importance. By its solution the large brown coal deposits in various countries will be made available for large scale hydrogenation.

After experimenting for many years, this problem is satisfactorily solved by the use of oxygen and the Winkler generator. Gasification takes place at about 1000° C. Depending upon the gasification medium, this apparatus can be used to generate fuel gas, as well as a mixture of nitrogen and hydrogen or a water gas almost free of nitrogen for the methanol syntheses. Only air, or air with a little steam, is used for fuel gas, and a mixture of 50-50% oxygen-nitrogen, to which steam is added, for the ammonia synthesis. Pure oxygen mixed with large quantities of steam is used to generate hydrogen. The brown coal is completely gasified in this process and only very small quantities of hydrocarbons are present at these high temperatures. The Winkler generators at Leuna generate 75000 m^3/h.

Another interesting possibility for producing hydrogen, of particular importance for the hydrogenation of coal, petroleum and tar, is based on the splitting of gaseous hydro-carbons as found in the waste gases from these processes, as natural gas or as constituents of coke oven gas.

I.G. has developed both processes. It has been found that the splitting of steam is the most satisfactory for large scale production. The conversion requires very high temperatures, which can be held within reasonable limits only by suitable catalysts. Even so, 800° C are necessary for a satisfactory and speedy reaction. Reduced nickel activated with various additions is a particularly suitable catalyst. One characteristic of the nickel catalysts is their high sensitivity to sulfur. Only little more than 10 mg sulfur/m^3 cause poisoning. Organic sulfur compounds found in many gases are just as harmful as H_2S, and a way had to be found to remove them. The only feasible solution so far is based on the catalytic splitting in H_2S, which can be removed by known methods.

Besides the production of gases, their cleaning posed a number of problems, differing for the three processes and depending upon the degree of cleanliness required. The ammonia synthesis requires a gas entirely free of H_2S and CO, to avoid poisoning the catalyst. The CO-H_2 mixture for the methanol synthesis is carefully freed of H_2S. To be sure, the catalyst is less sensitive to sulfur than the ammonia catalyst, but only small quantities of sulfur damage the copper in the methanol converters. The gasoline synthesis requires the least pure hydrogen. The catalyst and apparatus are sulfur proof and CO admixtures are troublesome only because they are converted to methane by hydrogen.

The water gases produced by these methods are cleaned in several successive stages. Their principal constituents are H_2 and CO and they are always polluted by H_2S, depending upon the sulfur content of the raw material used. To remove the CO, it is converted to CO_2 and H_2 by catalytic conversion with steam. This conversion is made as completely as possible in the ammonia and gasoline syntheses, but only to the extent of the required proportion of CO and H_2 in the methanol synthesis. Though this process is not particularly sensitive to sulfur, the processing of gases free of sulfur has many advantages, so that it is generally advisable to clean the H_2 for gasoline production of its sulfur.

For the sulfur-poor coke water gas we have developed the generally known method of desulfuring with active carbon. This process requires more extensive equipment for gases with high sulfur content, such as brown coal gases. In the search for improvement we recently succeeded in finding organic liquids, which combine with the H_2S when cold and give it off again when hot. Gases rich in sulfur are first cleaned in this manner and then conveyed to the carbon unit for complete desulfuring.

To remove the CO_2 the gases are washed with water at increased pressure. The last cleaning stage for the ammonia synthesis gases consists of washing with a solution of cuprous-oxide @ 200 atm., in which residual traces of CO and CO_2 are removed. This fine cleaning may be omitted for the methanol synthesis and the hydrogenation of coal, petroleum and tar for reasons already mentioned.

Another process is the well known decomposition of coke oven gases by freezing. The production of hydrogen poor in nitrogen for the methanol and gasoline syntheses requires a special modification of this process. Hydrogen can also be obtained from coke oven gases for these purposes by the catalytic splitting described herein.

Let us now consider the economic side of hydrogen production. Table 2 shows the raw material and power requirements for the production of 1000 m^3 cleaned hydrogen by various processes and compressed to 200 atm. The power requirement includes auxiliary power and manufacturing steam, converted to kWh.

Table 2.

Raw Material and Power Requirement for 1000 m^3 Hydrogen @ 0° C and 760 mm Hg, cleaned & compressed to 200 atm.

PROCESS	Consumption			
	Coke kg.	Br. Coal with 50% H_2O, kg.	m^3 Gas, kcal × $10^3/m^3$	kWh
Coke water gas, intermittent	700	--	--	800
" " " with O_2	540	--	--	950
Brown Coal water gas with O_2	--	1900	--	1000
Coke oven gas freezing	--	--	2700	1000
Hydrocarbon decomposition with steam	--	--	3200	800
Hydrogen electrolysis	--	--	--	6300

These figures are, of course, only mean values, subject to fluctuations with the character of the raw materials and the efficiency of the plant. In spite of this, the figures are interesting. They show, e.g. that in the oxygen gasification of coke the saving in coke is at the expense of increased power consumption compared to the old process. There is a similar comparison between the coke oven gas decomposition and the hydrocarbon decomposition. Decomposing the coke oven gas requires more power for compression, while the hydrocarbon decomposition requires heat energy for splitting. And finally, if we compare the hydrogen electrolysis with the other processes, we can see that electrolysis can be considered only where extraordinarily cheap power is available.

Although raw materials and power represent the major items of the cost of hydrogen, it would be a mistake to compare the various processes on this basis, because its use, maintenance, cost of plant and repairs also play an important part. Only by considering all these factors can we intelligently select the most economical process for the production of hydrogen.

From the production of hydrogen we now come to hydrogenation proper and its problems, which exceed those of hydrogen production in their multiplicity.

The most important of these problems has always been the catalyst, since its effectiveness is a determining factor in the choice of pressure and temperature, as well as the dimensions of the reactors.

It is still impossible, at this time, to predict a suitable catalyst for a given process. We are, therefore, still dependent upon a systematic search for the best catalyst. Thousands of catalysts have been examined for their ability to speed up and control reactions and their resistance to chemical and physical influences.

The present day ammonia catalyst consists of metallic iron of especial purity activated with small quantities of alkali and aluminum oxide.

While the problem of the ammonia catalyst is chiefly the speeding up of the reaction, that of controlling the reaction is added to it in the methanol synthesis. Table 1 shows the formation of isobutyl alcohol and methane as a possible side reaction of this synthesis. But numerous other possibilities for conversion exist, which may produce higher hydro-carbons, alcohols, aldehydes, cetones and acids.

The basic substance of the methanol catalyst is oxidic. Zinc oxide activated with chromic acid is used. Our experiments showed that very close limits in composition must be held to for satisfactory control of the reaction. Very slight deviations will cause side reactions.

We experienced our greatest difficulties in the development of catalysts for the hydrogenation of coal. The process works in two stages. In the first stage the reduction of the coal is aimed at, by which we understand the splitting up of the high molecular hydrocarbon compounds by the absorption of hydrogen. At the same time we must also try to combine other constituents of the coal, such as oxygen, sulfur and nitrogen, which must not be contained in the gasoline, with hydrogen, so that they may be separated by themselves. In the second stage the hydrocarbons formed or the middle oils produced from petroleum and tar by pre-hydrogenation are converted into gasolines by further splitting up and hydrogenation. To do this the catalyst must not only be in a position to speed up splitting and hydrogenation reactions, but also to control them so that they will take place together in the proper time. If the splitting effect is too strong, unsaturated hydrocarbons and products of condensation are formed. On the other hand, if hydrogenation is too strong, methane may preferably be formed with high hydrogen consumption and development of heat. The combination of the other constituents with hydrogen must also take place at the same time. A further difficulty is represented by the fact that the sulfur contained in the coals is generally an active poison.

The increase in decomposition was of decisive importance to the hydrogenation of coal. Decomposition without a catalyst is possible under the most favorable conditions of reaction only to the extent of about 60% and only the development of suitable catalysts has made it possible to decompose the coal 95%. Other improvements in the process, however, are partly responsible for these results. It was found, e.g. that the alkalinic ashes of brown coal act as negative catalysts and strongly retard decomposition. This difficulty was overcome by treating the coal with acid to neutralize the ash.

The proper application of the catalyst, too, greatly influences the decomposition. To get a high catalyst effect the coal is impregnated with a catalyst solution, and it was a difficult engineering problem to develop suitable mixing and proportioning devices, which would assure uniform distribution.

In the search for catalysts the sulfides of iron were found, at first, to be suitable. Then it was found that catalysts containing metallic oxides of the 6th group, which are transformed into sulfides in the course of the process, or more active. Later it proved advantageous to use these catalysts as sulfides of special structure from the start, and their effectiveness could be considerably increased thereby. The basic substances of catalysts today are iron, tungsten and molybdenum.

Closely connected with the development of the catalysts is the development of the apparatus for hydrogenation, since the catalyst has an important bearing on the pressure and temperature relations and the dimensions of the reaction space. There are various points of similarity in the design of reactors for the 3 syntheses. As shown in Table 1, considerable heat is developed in the absorption, or deposition (Anlagerung), of hydrogen. If this heat is not taken away, the temperature in the reaction space will rise rapidly. But the equilibrium is displaced to the detriment of the product with rising temperature. Besides, in the methanol synthesis and, in particular, the gasoline synthesis, care must be taken to hold these reactions within very close temperature limits. Exceeding those limits may cause side reactions, which develop much more heat than the process proper. The temperature may rise very rapidly, the converter may run away and cause heavy material damages or even catastrophes of the worst kind.

One possibility of temperature control is by the kind of gas supply. The catalyst space may be flushed with gases which will carry off the heat of reaction. A very careful development of the gas supply system closely suited to the heat of reaction of the process is necessary to maintain a safe heat equilibrium in the converter. Constant heat generation is a prerequisite for this, which, in turn, is dependent upon the conversion and, in the final analysis, on the unchanging effectiveness of the catalyst. This method of temperature control was used in the development of the ammonia and methanol syntheses and lead to the development of tube converters.

Further possibilities of heat regulation exist in the recycling of the products of reaction and the addition of cold gas in various zones of the reaction space. Changing the rate and speed of feed may also be used for regulating the heat. The last two methods are of particular importance to heat control for the hydrogenation of coal in the liquid phase.

Heat exchange is closely connected with temperature regulation. In order to simplify the process we must try to cover the heat losses by the heat of reaction, which requires a high conversion and very good heat exchange.

The last problem to be discussed is that of construction materials. We had found a way to overcome the effects of hydrogen in the ammonia synthesis by lining the converter jackets with a hydrogen-resistant material. In the methanol synthesis the effect of CO on the ferrous materials was added to the problem, Iron carbonyl was formed, which caused heavy damages and poisoned the catalyst. The products of corrosion were carried off in gaseous form. It was necessary to find a lining material that would resist both the hydrogen and the CO. We have succeeded in developing a Cu-Mn-alloy, which satisfactorily meets these requirements.

In the hydrogenation of coal, two main difficulties had to be overcome. In the first place, we had to resist the combined attack of hydrogen and sulfur. Temperatures of about 500° C are used in this process, at which ferrous sulfide is formed, destroying the material and forming encrustations of ferrous sulfide. These cause fouling of heat exchangers and thereby reduce heat recovery. In the search for relief our metallographists finally discovered the suitability of a zinc coating, which, however, does not consist of a thin layer as applied in ordinary galvanizing, but of a diffusion layer of zinc-iron mixed crystals, obtained by a lengthy treatment with hot zinc vapors.

The second main problem was to find a material of sufficient strength at high temperatures, that would also resist the chemical attacks of H_2S and H_2. A combination of these properties was found in chromium steels containing small quantities of Mo and V. These alloys were later improved by the addition of tungsten. This material today resists the combined effects of high temperatures and pressures and of H_2 and H_2S in continuous operation.

Now that I have outlined the problems of industrial hydrogenation in rather bold strokes by examples of the ammonia, the methanol and the gasoline syntheses, I shall again summarize in Table 3 the various differences in the three processes. You will first observe the gases required for carrying out the syntheses, whose constituents co-determine the choice of the hydrogen process. Beside these are the harmful constituents which must be removed in cleaning the gas. In the last column are the undesirable constituents which lead to unpleasant concentrations in the circulating systems of the syntheses and cause hydrogen losses.

The section of catalysts shows the rising demands on them, from the speeding up of the reactions and their control to the manifold tasks of the catalysts in the gasoline synthesis, and it may be observed how the increasing problems were solved by the development of metallic, oxidic and sulfidic catalysts. The last column of this section shows the increasing demands on the construction materials, which are a maximum in coal hydrogenation, where heat resistance and resistance against H_2 and H_2S attacks are required at the same time.

Table 3

Hydrogenation Process	Synthesis Gas Required	Synthesis Gas Harmful	Synthesis Gas Undesirable
Ammonia Synthesis	H_2, N_2	CO, H_2S	CxHy
Methanol "	H_2, CO	H_2S	CxHy, N_2
Gasoline "	H_2		CxHy, N_2, CO

Catalysts

Task	Basic Substance	Material Resistant Against:
Speed-up Reaction	Metallic	H_2 & Temp.
" " & control Reaction	Oxydic	H_2, CO & Temp.
Simultaneous Speed-up of Splitting & Hydrogenation Reactions	Sulfidic	H_2, H_2S, Temp. & Press.

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HYDRO. DEMON. PLANT DIV.

KC Braun
1/17/47

200 BARRELS/DAY HYDROGENATION DEMONSTRATION PLANT AT LOUISIANA, MISSOURI

(Suggested arrangement by Dr. Frese, Jan. 17, 1947).

Certain considerations regarding safety, trouble-free operations and cost of construction appear of considerable importance to me. On the attached sketches I should like to call attention to these basic considerations.

1. High Pressure Stalls.

Each stall here consists of 3 sections, a converter section, a preheater section and a section containing the cold catch pot cooler, the catch pot itself, and the circulating gas washer. The sections themselves are protected on 3 sides by reinforced concrete walls while the back side is left entirely open for the rapid escape of gases.

In all German plants only the hot convertor section was enclosed by concrete walls, while the preheater section and the cold apparatus, such as the catch pot and washer, were outside of the stall. To be sure, most German plants had a concrete back wall, which however, extended only to about 1/3 of the height of the other walls and had an inter-changeable heavy wooden door in the middle.

No doubt, the plant planned for Louisiana offers a greater factor of safety. However, no trouble need be expected in the cold sections, if it is properly and carefully installed. Throughout many years of experience I have known of only one case where a fire of considerable proportions occurred due to a leak in a small valve on a separator in the circulating gas line between the control room and the stall. A large portion of the cold high pressure lines (all gas circulating lines with separators, cold gas lines, product lines, etc.) with all valves must be located, unprotected, in the open, in any case. The possible saving in cost, if the third cold catch pot section were located in the open, should receive careful consideration. From the standpoint of safety this would be entirely justified.

It is difficult to decide on the best location of the pumps of the hot circulating system between the hot catchpot and the preheater. This equipment, with its lines conveying hot materials containing solids, is dangerous in itself, particularly at mistakes in operation and requires considerable apparatus with a large number of valves. In Germany, this equipment was located on the back wall of the stalls. To locate this equipment on the front wall of the stall, between the control room and the stall, would involve considerable danger. We should attempt, by all means, to protect this equipment by concrete walls by locating it inside of the cold catch pot section, whereby this section would still serve a good purpose. If there is no room for it there the relocation elsewhere of some cold, safe unit, washer or catch pot, should be considered.

2. High Pressure Lines, Gas Circulating.

For reasons of safety and saving in cost, all high pressure lines conveying products and gas should be as short as possible. This is particularly true of the gas circulating system, because the comparatively long line represents an important cost item. An expansion joint should be in this line. If it is intended to operate the liquid phase separately from the vapor phase, Sketch 2 shows a proposed arrangement. The lines shown dotted must be added. The gas circulating line is properly located parallel to the wall of the pump house. The valve maintaining pressure difference should be located in the control room.

3. Pump House.

In consideration of the point of view expressed herein on the location of the lines, it is probably best to lay out the longitudinal wall of the pump house parallel to the front of the stall and the control room. The pumps should be so arranged that the lines are shortest, i.e. the pumps should be closest to the equipment they serve. Pumps serving similar purposes, such as water injection pumps, should be grouped together. All lines conveying product should be properly laid in a trench with steel grating cover thru the control room to the high pressure stalls.

The sketch shows the pumps arranged from right to left in the following order: gas circulating pumps, middle oil injection pumps for vapor phase, water injection pumps, flushing oil pumps, light naphtha injection pumps, coal paste presses, and wash oil pumps for circulating gas washer. This layout merely represents a basic arrangement details must be considered when detail drawings are made.

4. Coal Preparation.

The coal preparation and pasting building should be properly located near the high pressure paste presses, in order to make the heat jacketed coal paste circulating line as short as possible. The sketch shows 3 paste tanks. I consider 3 tanks of 25-30 m^3 capacity, 2 for preparing the paste and one as an equalizing tank from which the paste is conveyed to the stall in a recirculating line, better than 2 tanks of 10 and 60 m^3 capacity. The tanks should be so interconnected that they could be interchanged at will in case one is out of service.

5. Centrifuge and Let-Down Bldg.

This building, with the Laval centrifuges and the expansion vessels for the HOLD, should properly be located near the liquid phase stall and the coal preparation building. The kilns should be located near the centrifuge building.

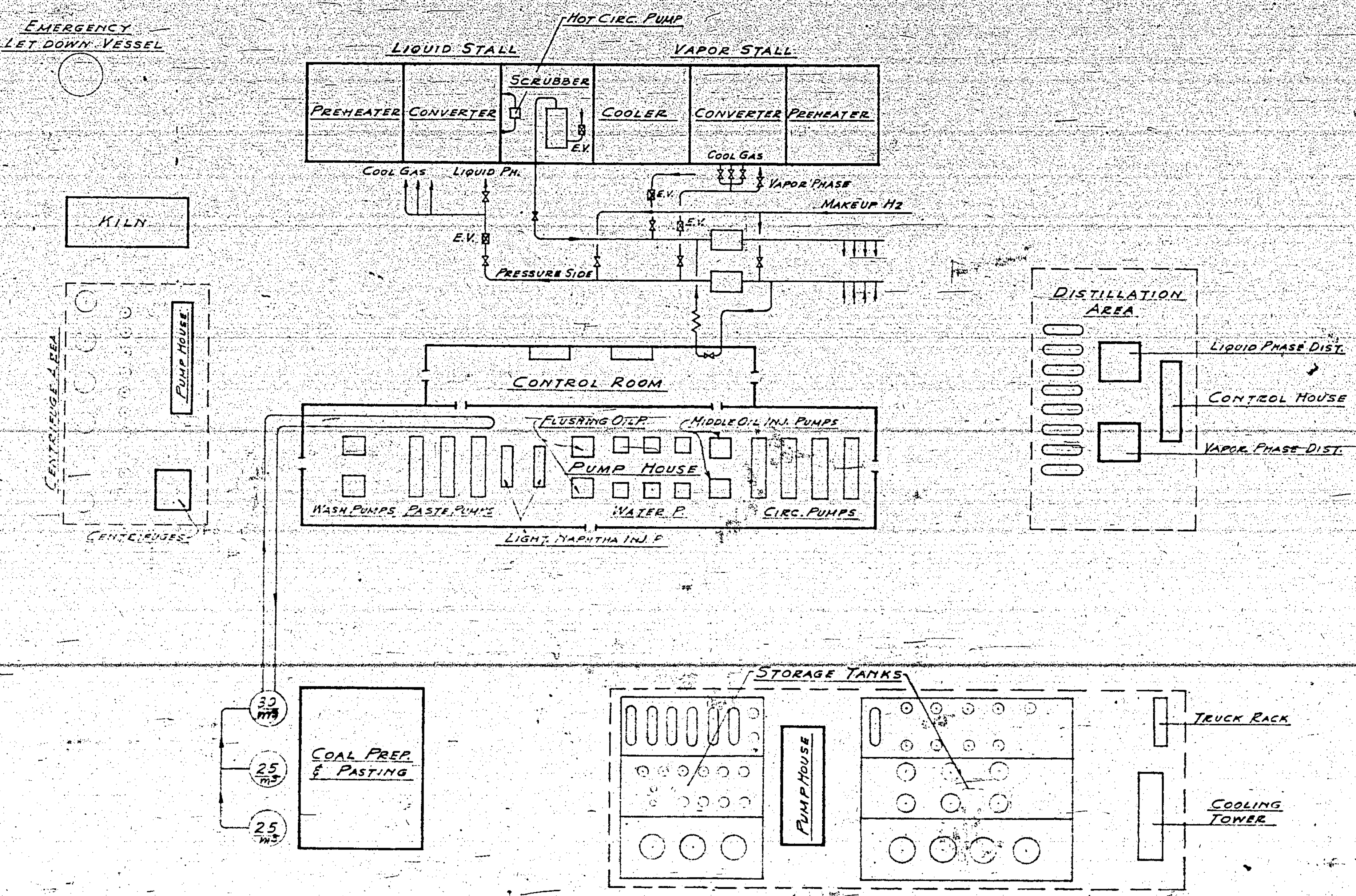
6. Distillation and Tank Storage.

These should be located on the corresponding other 2 sides of the pump house.

7. Emergency Let-Down Vessel.

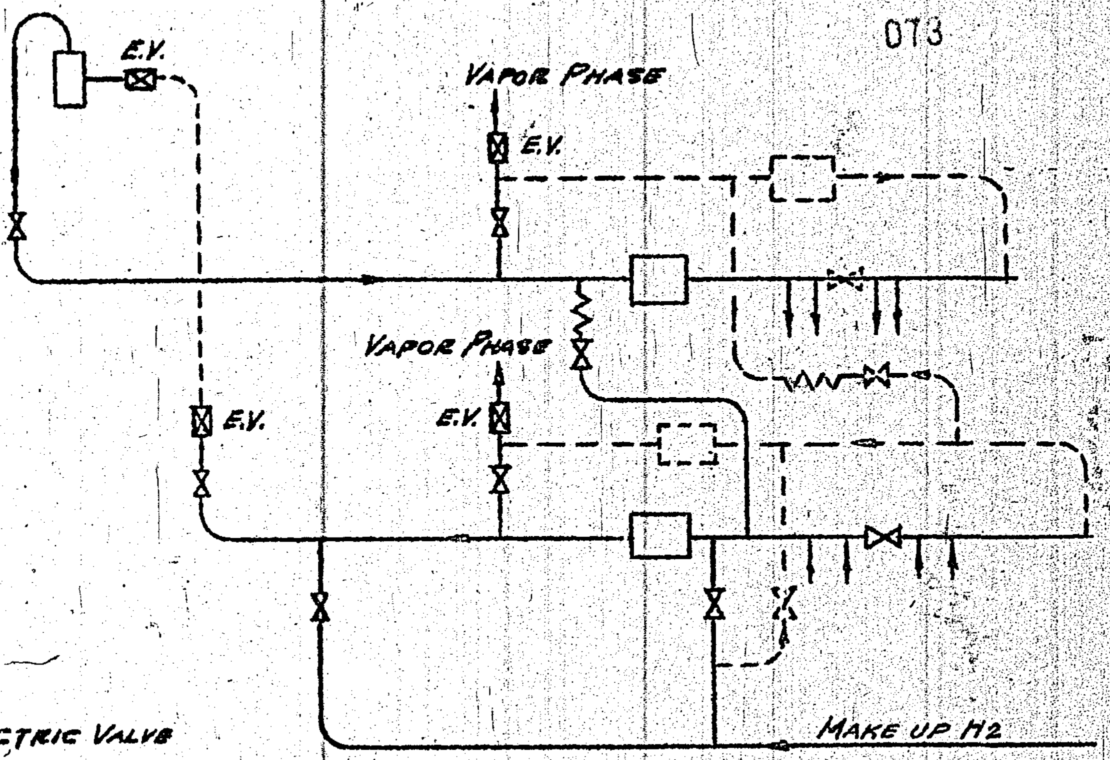
This should be located near the liquid phase stall so that the high pressure expansion line from the stall is not too long. In sudden decompression this line gets very hot and a good expansion joint must be provided to permit linear expansion and prevent leaks. The sketch shows the vessel to the left of the liquid phase stall, a suitable distance from the preheater section. The fire in the preheater is always extinguished before emergency expansion.

T-215
SKETCH-1



SUGGESTED ARRANGEMENT OF HYDROGENATION
DEMONSTATION PLANT AT LOUISIANA

LEGEND:
E.V. ELECTRIC VALVE



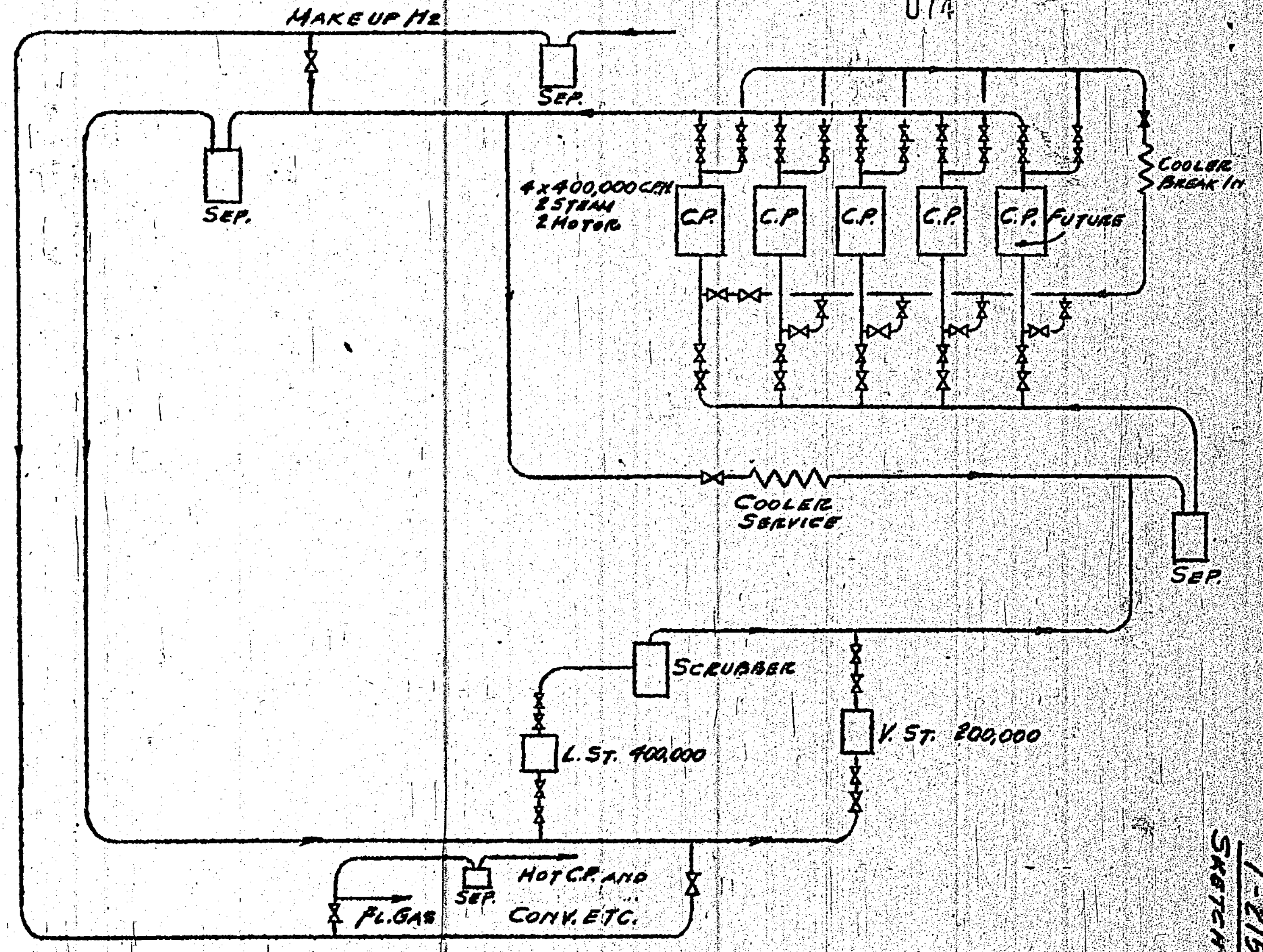
E.V. - Electric Valve

Alternate Circulating Gas Systems
If 2 Circuits are Desired

T-215
Sketch 2

074

T-215
Sketch 9



GAS CIRCULATION SYSTEM

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HYDRO. DEMON. PLANT DIV.

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5/21/43

DETERMINATION OF CONCENTRATION OF PASTES WITH BRABENDER PLASTOGRAPHS.

Operation controls have obtained a "Brabander Plastograph" for a continuous supervision of the paste produced. Principle and Nomenclature. This apparatus is intended for the continuous measurement of the quasi-viscosity of a branched stream of the paste.

Under certain conditions there exists a connection between the quasi-viscosity and concentration, in that the viscosity and concentration, in that the viscosity of more concentrated pastes is higher. The special conditions in our case are the following:

1) Viscosity must be always measured at some definite constant temperature, (as in the case of true viscosity).

2) the size distribution of the pasted powder must remain constant.

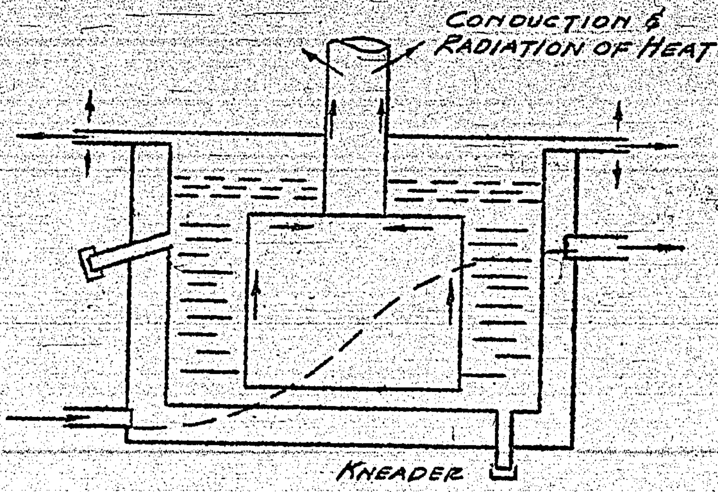
3) the viscosity of the pasting oil used must remained unchanged.

4) no separation of the components must take place during the measurements.

In the preliminary experiments run, only the last three requirements were approximately adhered to. The requirements of a constant temperature were not met however, for reasons to be given below, in spite of the use of thermostats. A constant temperature must be considered as a principal requirement in all viscosity determinations, and especially so with substances such as our pastes. A paste at 50° C is four times as viscous as at 70°, i.e. very small changes in temperature result in enormous changes in viscosity. This experimental error had to be definitely eliminated before even thinking about further investigations.

With regard to nomenclature, we should mention, that the name "plastograph is somewhat misleading. What is meant, is an instrument for measurement of higher viscosities.

Description of the Plastograph (Original Form). A roller is rotated at a constant speed of 56 r.p.m. in a pot with the paste (the kneader), 19x13 cm in size. A larger resistance (and therefore also a greater sensitivity) is obtained by staggering teeth on the outside of the roll and the inner surface of the pot. When used for operation control, the paste was made to pass through the pot upwards through two nipples; for laboratory testing, these nipples are closed with caps. (fig. 1).



PLASTOGRAPH, OIL MODEL
SCHEMATIC

FIG. 1

Heating is done in an oil filled thermostat of the Hoppler type.

The rotational resistance (which is proportional to viscosity) is measured by means of a so-called electrodynamometer connected with the pot over two ball bearings by means of a coupling (fig 2, No. 8). The dynamometer consists of a synchronous motor, 1, mounted on a swinging suspension. All resistance met by the teeth of the kneader inside the paste will be manifested as a force in the casing of the motor, and it will tend to rotate the housing in a direction opposite the direction of rotation of the anchor. These moments of rotation, damped by an oil damper, 4, are transferred by means of a system of levers (3) to the measuring part (5, 6). Several large weights (7), which serve as initial load, permit extending many fold the range of measurements.

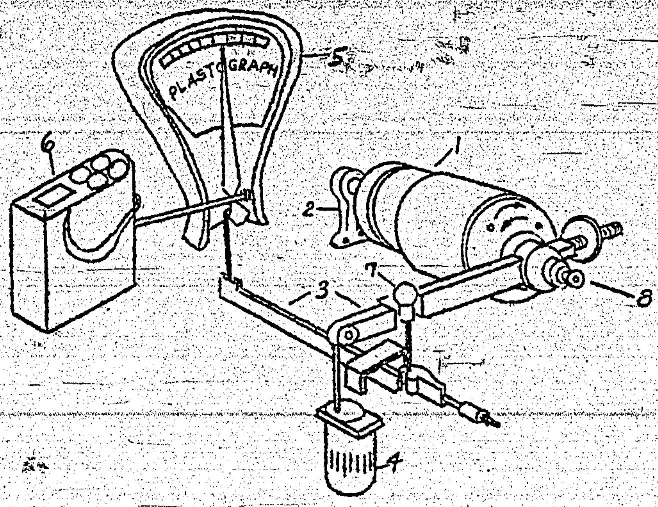


FIG. 2 ELECTRODYNAMOMETER FOR PLASTOGRAPH

The elegant and accurate electrodynamometer has not been changed by us in its essential parts, the thermal inadequacy of of the kneader caused us to make extensive changes in it. Viscosity values were found to vary widely, whenever a draft of air was produced. The reason for it can be found in the following facts of physics: the well conducting metal parts protruding out the paste, "suck in", under the changing outside conditions, varying amounts of heat from the paste, always more at first than furnished by the heat supply of the thermostat. There will be a temperature drop inside the mass of the paste. The parts adjoining the metal, in particular the toothed roll, will be especially strongly affected.

Constant conditions for viscosity evaluation might conceivably be produced by immersing the whole apparatus into a thermostat, say an air heated glass box. For some important reasons, the outside temperature will mostly be way below the thermostat temperature. In this case we would deal not with a static, but dynamic temperature equilibrium, i.e. the drop in temperature would remain, but would become constant. This means that determining the average temperature of the paste to establish a definite connection between temperature and viscosity, especially if the latter is expressed in absolute units is extremely difficult.

The location of the inlet and outlet nipples for the circulation of the oil through the thermostat proved to be an other source of erros. They were of the form shown in fig. 1, as frequently found on apparatus. A heat sensitive lacquer showed, that the zone underneath the S-shaped broken line was practically unheated, because oil simply choose the shortest way.

Plastograph (New Form)

A connection was accordingly made shown on fig. 3, (also on the large scale sketch, fig. 4): there are three inlet and outlet nipples in the thermostat. Two of them operate upon a nipple introduced at the bottom of the pot. From these the oil is symmetrically distributed above the hollow bottom and over the whole hollow side wall in six segments spaced at 60°.

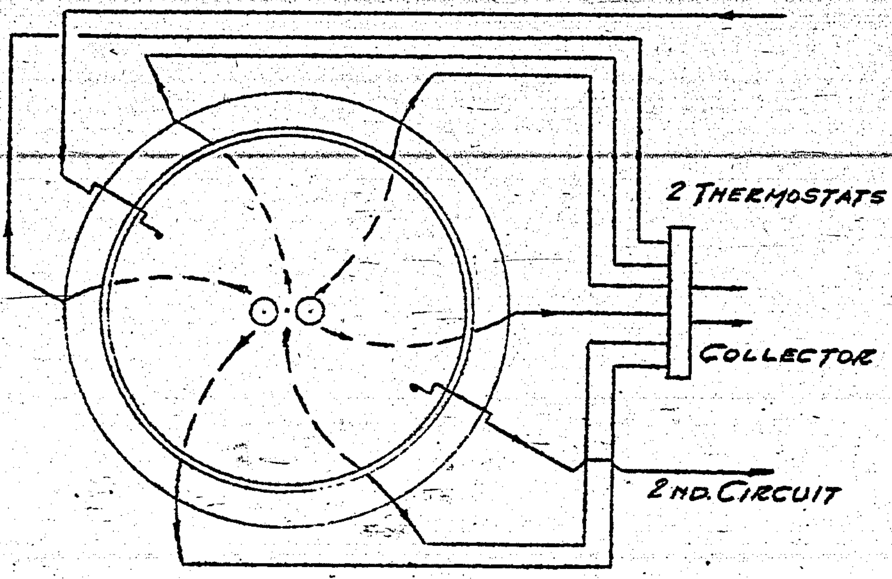


FIG. 3: PLASTOGRAPH, NEW MODEL
SCHEMATIC CONNECTIONS OF HEATING
OIL CIRCUIT

Outlet nipples distributed over the periphery conduct the oil through six hose connections into a glass collector with two outlets. The third thermostat connection is used to pass oil through a hollow metallic disk on top of the paste. In this way the only surface of the paste still remaining free was almost completely covered with a "top heating".

The heating oil was led in through a perbunan/perduran hose. This material is resistant to oil, and withstands long heating to 150°.

The principal change in addition to the ones above was the introduction of heat dams between the kneader and the retaining plate, as well as between the toothed roll and the power transmission. For the first task, we used the plastic "Mycolex" composed of powdered lead borate glass and powdered talc, which can stand a long time heating to over 300° C (being of purely inorganic composition) and which behaves largely like a metal when worked; the shaft of the toothed roll was made of V120 steel with a wall thickness of 1 mm, the weight of which was greatly reduced by a large number of holes, (an other shaft made of fused alumina with metallic end clamps is at present being made). The heat conductivity of V120 is 5 times smaller, than cast steel. The heat damming parts are shown in fig 4.

As a result of these precautions, one discharge with its corresponding heat radiation is largely avoided, so that each point of the paste is at the same temperature, almost identical with the oil heating.

In addition, a heated by-pass for the kneader was introduced in the kneader. This heated bypass, aided by a worm drive, produces slow circulation in opposite direction to the gravitational field, and prevents thus settling out of the paste, or a separation of the solids. The kneader consists of metal, and is surrounded by a wooden box, filled with glass wool. The oil inlet and outlet hose connections are combined into bundles and wound with asbestos cords.

Preliminary Thermal Experiments. The success of this careful work was striking. It has been found that there was in fact no relationship with the outside temperature, and that the paste assumed very closely the temperature of the oil bath. The figures below were obtained for the purpose of comparison the old with the new models.

Old Arrangement:

Oil	67.5	72.5	76.1	82.2	87.0	93.5	97.5	102.8	108.0	132.5°
paste	62.2	66.0	69.0	72.1	78.0	83.0	88.0	92.0	96.0	120.5°
d	-5.3	-6.5	-7.1	-10.1	-9.0	-10.5	-9.5	-10.8	-12.0	-12.0°

New Arrangement:

Oil	72.0	77.8	82.6	87.7	94.5	99.0	103.5	108.1	113.5°
paste	72.2	77.4	82.2	87.0	93.5	97.8	102.3	106.9	112.0°
d	+0.2	-0.4	-0.4	-0.7	-1.0	-1.2	-1.2	-1.2	-1.5°

The difference in temperature in two comparable measurements was up to 12° with the old model, and 1.5° by the new. Even this unimportant difference should disappear when the fused corundum shaft is introduced.

It is surprising, how little these thermal sources of error are recognized elsewhere. This fundamental error is present in a viscosimeter made by one of the leading apparatus manufacture nand introduced by them with considerable propaganda.

Connection with the absolute system of measurements. The scale of the plastograph reads in 0 to 1000 g (with additional weighing of the electrodynamometer even larger values), and this measures the resistance acting on the circumference of the toothed roll. These figures must be expressed in viscosity terms on the absolute scale. For this purpose very viscous transparent synthetic oils supplied by the I.G. Co. were measured in a Satz Ubbelohde viscosimeter, which permits direct measurements in the absolute system and was used for the standardization of the plastometer. The points obtained gave us the calibration curve (Brabender scale in centistokes).

Measurements of Paste. Measurements of viscosity of coal pastes showed, that when changes in concentration were quickly produced, the viscosity depended enormously on the concentration. It is not however true, that a certain viscosity corresponds to a certain concentration. Nor can this possibly be true, because years of observation have shown, that the fineness of grinding, measured by passing through a 10,000-mesh (0.06 mm), varies very greatly during a time interval of 24 hours. This must be attributed to the variations in the structure of the coal. Moreover, the second requirement, of a uniformity of the pasting oil, is not strictly met, because of variations in the solids and asphalt in it.

Measurements of viscosity are never the loss of interest in operation, because the errors to be observed are usually great, while changes in the fineness of the grind and in the composition of the pasting oil are continuous in character.

In actual practice this would result in slowly rising and falling viscosity curves, with irregularities in some parts. These irregularities call the attention of the operating department to some irregularities in the coal or oil supply.

Conditions are still more favorable with the soda and ammonium chloride pastes, because the fineness varies there less, the material as delivered being more uniform.

Additional Information. Should we compare viscosities of the Scholven and Gelsenberg pastes, we will be struck with the enormous drop between 50 and 70° in the Scholven curve, a behavior not shown by the Gelsenberg paste. The difference is probably caused by the high asphalt content of the Scholven coal paste. It is very probable, that with accurate data some interesting relationships will be discovered.

Summary. A kneader is developed in the Brabender plastograph, which corrects the thermal uncertainties. Only after such thermal errors have been eliminated can this instrument be a) useful in operation control, and b) offer promise of becoming adapted for finer laboratory measurements.

/s/ Tiedemann

Buer-Scholven May 13, 1943

W. M. Sternberg

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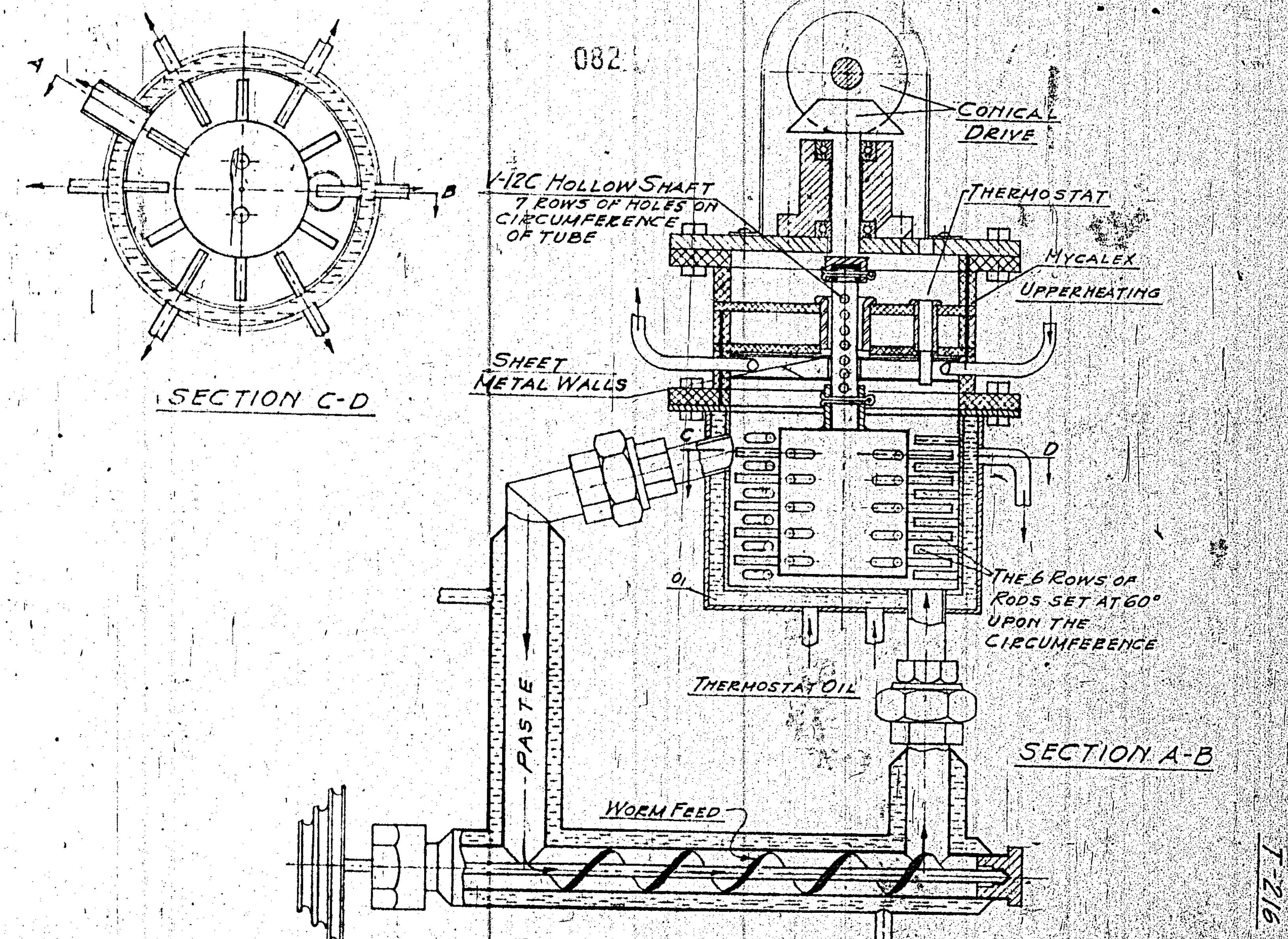

PLASTOGRAPH
FIG-4

SUMMARIZED REPORT ON THE COAL HYDROGENATION LIQUEFACTION OIL AT PRESSURES IN EXCESS OF 300 ATM., WITH RUHROL CATALYST K 413. (Jan. 25 - Apr. 4, 1941)

From Dr. Frese's Files

CONTENTS:

I. General Experimental Conditions.

1. Apparatus.

The converter consisted of a N8 tube, 45 mm i.d. and about 5.5 m. long. The volume of the catalyst was 5.3 liters. The whole length of the converter was heated with 3 electric heating units. Additional heaters were used for the bottom, the head of the converter and the lead from the preheater to the bottom of the converter. The inside temperature was measured in 6 places. The largest temperature difference of the six places was 0.3 mv.

A N8 tube, 6 mm i.d. and 12 m long was used as the preheater. It was set in a lead bath heated with gas. A 5 li high pressure container with a level indicated by a sight glass was used for a hot catchpot. The HOLD was continuously decompressed in a low pressure container. The released gas was measured in a gravity indicator and wet gas meter and twenty four hour average sample of it was taken with an automatic sampler. The product was withdrawn every half hour, measured and centrifuged. An average sample of 24 hour run was tested. In attempts to arrive at a balance, the gas dissolved in the product at atmospheric pressure was analyzed. The middle oil was injected with Hofer pumps, which operated perfectly during the test. The injection feed was filtered through a Bosch filter in front of the pump.

Temperature measurements were made with an iron-constantan thermocouple, with a cold junction at 40° C.

2. Catalyst.

The Ruhröl catalyst K 413 was used. It was in the shape of riffled 6 mm pills. The amount installed was 3.130 kg = 5.3 li. The test at present is still being continued, and dismantling results can not as yet be given.

3. Gas.

The tests were run with a make-up gas of the following composition:

H_2	98.2-97.4%
CO	0.1-0.3%
N_2	1.7-2.3%

The pressure in the beginning was 670 atm. The principal tests were run at 500 - 550 atm. In conclusion, a series of tests were run at 450 atm. The gas thruput was, independently of the injection, always 15 m³/hr. (constant time of contact, variable partial pressure of oil). The decompressed gas at the stall outlet was measured with a gravity indicator and gas meter. The automatic equipment permitted getting the average samples over 24 hours.

4. Injection Feed.

The tests were run with gasoline-containing and gasoline-free middle oils obtained in the liquefaction of bituminous coals, of which the Hydrogenation Works at Scholven furnished 10 and 2 m³, respectively. Short runs were made with gasoline-containing and gasoline-free middle oil from Upper Silesian coal from I.G. Farbenindustrie, Ludwigshafen, High Pressure Testing Section, and of which 200 li were available for our tests. Table 1 is a summary of the principal analytical results of the A middle oils.

Table 1.

	Ruhr coal Liquefaction Oils (Scholven)		Upper Silesia Coal Liquefaction Oils (I.G.)	
	Gasoline-Containing	Gasoline-free	Gasoline-containing	Gasoline-free
Spec. grav. at 15°C	0.934	0.972	0.903	0.965
Boiling point test Engler.				
St.	56	160	70	201° C
100°	7.7 vol.%	--	7.3 vol.%	--
170°	22.2 " "	0.5 vol.%	32.8 " "	--
200°	32.2 " "	8.0 " "	43.3 " "	--
300°	78.2 " "	82.0 " "	89.8 " "	92 vol.%
E.P.	98.5%/345°	98%/325°	98.5%/328°	99%/319°
Column Distillation -165°	25.2%	--	34.0%	--
Aniline point				
total	-21.8°	<-25°	-2.7°	<-25°
-165° (column)	+30.2°	--	+28.0°	--
Phenol	12.2%	13.4%	13.8%	19.8%
Pyridine	2.9%	2.6%	1.9%	2.0%
Ultimate Analysis:				
C	87.5%	86.3%	85.1%	85.1%
H_2	10.2	9.3	10.6	9.5
S	0.08	0.09	0.16	0.024
Cl	0.003	0.004	0.004	0.004

The A middle oil was never injected alone, but always with B middle oil produced in the test. During the starting period, and until the stall reached equilibrium, there was always enough B middle oil available from previous runs. During this time the tests were run with 50% parts of A middle oil and 50 parts of B middle oil. After equilibrium had been reached, the injection feed was adjusted to the same amount of B middle oil as obtained in the catch pot, while the amount of A middle oil was equal to the amount of gasoline in the catchpot, plus gasification.

Analyses of the B middle oil, which naturally depended on the conditions of the tests, are given in section III.

5. Duration of Experiments.

The total time spent in experiments at pressures exceeding 300 atm. was 70 days (Jan. 25 - Apr. 4, 1941).

The test is at present still being continued at 300 atm. Experimental conditions during the test were:

Days	Injection Feed	Temperature mv	Pressure atm	Thruput kg/liter/hour
1	no injection	heating up	670	0.0
2	" "	24.0	"	"
3	Scholven gasoline + m.o., with own B oil (50:50)			
4	" "	25.0	"	0.5
5	" "	"	"	0.8
6	" "	"	"	1.0
7	" "	"	"	1.2
8 - 11	" "	"	"	1.5
12 - 13	" "	25.3	500	"
14 - 22	" "	25.5	"	"
23 - 25	" "	"	"	1.0
26 - 28	" (60:40)	26.0	535	"
29 - 35	" "	"	"	1.5
36 - 46	" (65:35)	26.5	540	"
47 - 58	Scholven m.o. with own B oil (60:40)	"	550	1.0
59 - 60	Upp. Sil. m.o. with B. oil from 56-58 day. (60:40)	"	"	"
61 - 63	Upp. Sil. B m.o. + B m.o. from 59-60 days (60:40)	"	"	1.3
64 - 70	Scholven m.o. - local B m.o. (60:40)	"	450	1.0

II. Description of Experiment.

1. Tests with Gasoline-Containing Middle Oil From Scholven: (14-th to 46-th days of test).

The starting period (7 days) and the time while equilibrium in the stall was being reached (7-th to 13-th days) will not be considered here.

Beginning with the 14-th days the B-product returned into the cycle was in equilibrium. The tests were run until the 46-th day with gasoline-containing middle oil from coal liquefaction at varying temperature and thruput.

The correlation of the production and of the analytical results in the catchpot with the temperature and thruput are shown in table 2.

Table 2.

Tests with Gasoline-Containing Scholven Middle Oil. Production vs. catchpot analysis and experimental conditions.

Temperature, mv.	25.5		26.0		26.5
Thruput li/kg/hr	1.00	1.45	1.00	1.45	1.45
Pressure, atm.	500	500	535	535	540
Days of test	3	9	3	7	11
Yield, kg -165° gasoline/li/hr	0.46	0.58	0.51	0.65	0.68
Sp. gr., 15°	0.830	0.844	0.820	0.837	0.832
Distilled over, below 165° Still	54	50	62	53	58
Aniline point, °C -165° (no gas. gasol.)	16	19	16	18	15
Aniline point, °C >165°	-12	-13	-15	-17	-22
Aromatics in -165° gasoline, % vol.	42	40	42	40	42
Vol. % below 100° in -165° gasoline	47	43	48	46	46
% phenol in catchpot (by weight)	0.2	0.5	0.2	0.6	0.5
Weight % pyridine in catchpot	0.02	0.05	0.01	0.07	0.06

2. Tests With Gasoline-Free Middle Oil From Scholven

(47-th to 58-th and 63-th to 69-th days)

The tests were first run at 550 atm. and later at 450 atm, to have conditions similar to parallel runs in I.G. Ludwigshafen. Results are given in Table 3.

Table 3.

Tests with gasoline-free middle oil from Scholven. Production vs. catchpot analysis and experimental conditions.

Pressure, atm.	440	450
Temperature, mv	26.5	26.5
Thruput, kg/li/hr	1.00	1.00
Days of test	12	7
Yield, kg -165° gasol./li/hr	0.48	0.41
Sp.gr., 15°	0.826	0.842
Distilled below 165°	60.0	52.0
An. pt, °C -165° (no gas. gasoline)	13	11
An.pt.>165°	-17	-19
Aromatics in -165° gasoline, in vol.%	45	47
% by volume below 100° in -165° gas.	47	45
Weight % phenols in catchpot	0.3	0.4
Weight % pyridin in catchpot	0.02	0.03

3. Tests with Gasoline-Containing and Gasoline-Free Upper Silesian Bituminous Coal Middle Oil (59-th to 63-rd days).

We had only 200 liters samples of the middle oil, and tests with this injection feed were only run for 2 days. Experimental results are not conclusive because during this short time no return with the middle oil produced was possible. The experimental results are shown in Table 4.

Table 4

Tests with Upper Silesian Coal. Production vs. Catchpot Analysis and Experimental Conditions.

	Gasoline-containing Middle oil	Gasoline-Free middle oil
Temperature, mv.	26.5	26.5
Pressure, atm.	550	550
Thruput, kg/li/hr	1.32	1.10
Days of test	2	2
Production, kg -165° gasoline/li/hr	0.70	0.52
Sp. Gr. 15°	0.818	0.828
Fraction distilled below 165°	63	61
An. pt, °C -165° gasoline (no gas. gasoline)	18	13
an.pt 165°	-10	-17
Vol. % aromatics in -165° gasoline	41	45
Vol. % -100° in -165° gasoline	46	45
Weight % phenols in catchpot	0.4	0.5
Weight % pyridine in catchpot	0.02	0.03

III. Analysis of Liquid Products of Reaction.

The principal analytical data of the gasoline and B middle oil distilled from the catchpot with different injection feeds with varying experimental conditions are summarized in Table 5, 6 and 7. The analytical methods are the ones prescribed for aviation gasoline (B.V.M.). The octane number was determined with the I.G. motor by the motor method. For the octane number tests with the overload motor during the operation with gasoline-free and gasoline-containing Scholven middle oil, 400 liters of refined and of stabilized gasoline were produced and sent beginning of April to the D.V.L. Results of the tests were not yet available when writing this report. The complete D.V.L. analytical results are summarized in Table 7.

Table 5.

Analyses of the Gasolines and B middle oil in Tests with Gasoline-containing middle oil, Scholven.

Temperature, mv	25.5	26.0	26.5
Thruput, kg/li/hr	1.45	1.45	1.45
Pressure, atm.	500	535	540
Test taken on	16-th	31-st	41-st day of run
-165° Gasoline			
% by Vol. in Catchpot	52	53	58
Sp. Gr., 15°	0.775	0.772	0.773
ASTM distillation			
St.	42.0°	38.0°	38.0°
% by vol., -100°	42.5	48.0	49.5
E.p.	97 %/168°	97.5 %/164°	98.5 %/166°
Aniline point, °C	+19	+18	+16
Iodine number, Hanus	3.5	4.4	4.1
Aromatics - olefines, % by weight	41	40	42
C	87.7 %	87.3 %	87.9 %
H_2	12.3 %	12.7 %	12.1 %
Octane number (mot. meth.)			
Not leaded	77.0	77.0	78.0
- 0.05% by vol.	85.5	86.0	87.0
- 0.12% by vol.	89.0	89.0	90.5
B Middle Oil > 165°			
Sp. Gr. 15°	0.907	0.913	0.917
Aniline point, °C	-14°	-13°	-22°
C	89.4 %	88.9 %	89.3 %
H_2	10.3 %	10.6 %	10.2 %

Analysis of Gasoline and B Middle Oil in tests with the Scholven Gasoline-Free Middle Oil.

Table 6

Temperature, mv	26.5	26.5
Thruput, kg/li/hr	1.0	1.0
Pressure, atm.	550	450
Test Taken on	56-th	67-th
	Gasoline - 165°	
% by Volume in Catchpot	59	51
Sp. Gr., 15°	0.775	0.777
ASTM Distillation		
St	36.0°	39.0°
Vol. %, -100°C	48.0	45.5
E.p.	96.5 T/164°	97.5 %/167°
Aniline point, °C	+13	+12
Iodine Number, Hanus	2.8	3.6
Vol. %, Aromatics + Olefines	45	47
C	88.0%	88.0%
H_2	12.0%	12.0%
Octane Number (mot. meth.)		
Not Leaded	79.0	79.5
+ 0.05% by vol.	87.0	87.5
+ 0.12% " "	90.5	90.5
	B - Middle Oil	
Sp. Gr., 15°	0.905	0.914
Aniline Point, °C	-17	-19
C	89.2%	--
H_2	10.2%	--

Analyses of Gasoline and B Middle Oil from Tests with Upper Silesian Coal Liquefaction Oils.

	Gasoline-containing Middle Oil	Gasoline-Free Middle Oil
Temperature, mv	26.5	26.5
Thruput, kg/li/hr	1.32	1.10
Pressure, atm.	550	550
Test taken on	62-nd	60-th day
	-165° Gasoline	
% by Vol. in Catchpot	62	59
Sp. Gr., 15° C	0.759	0.774
ASTM Distillation:		
St	36.0°	34.0°
% by Vol. -100°	47.5	45.0
E.p.	96.5 %/164°	97.5 %/166°
Aniline Point, °C	+ 18	+ 13
Iodine Number, Hanus	3.3	3.6
% by Vol., Aromatics + Olefines	41	47
C	87.3 %	87.5 %
H_2	12.7 %	12.5 %
Octane Number:		
Not Leaded	76.5	79.5
+ 0.05% by Vol.	85.5	87.5
+ 0.12% by Vol.	89.5	90.5
	B Middle Oil, > 165°	
Sp. Gr., 15°	0.898	0.903
Aniline Point, °C	-11	-19
C	89.3%	87.9%
H_2	10.4%	10.8%

Analysis of Gasolines Tested by D.V.L. in Overload Motors.

Injection Feed:	Scholven Gasoline-Containing Middle Oil	Scholven Gasoline-Free Middle Oil
Temperature, mv	26.5	26.5
Pressure, Atm.	540	550
Load	1.45	1.0 /day
Test Taken from Runs on	43-rd to 46-th	53-rd to 58-th
Sp. Gr., 15° C	0.779	0.783
Vapor Pressure at 37.8 atm.	0.42	0.41
Boiling point Analysis (ASTM)		
St	41.0° C	43.0° C
5% by vol.	63.0 "	64.0 "
15 " "	77.5 "	78.0 "
25 " "	85.5 "	86.0 "
35 " "	92.0 "	92.5 "
45 " "	98.5 "	100.0 "
55 " "	105.0 "	107.5 "
65 " "	113.0 "	116.5 "
75 " "	123.5 "	126.5 "
85 " "	136.0 "	141.0 "
95 " "	158.0 "	164.0 "
E.p.	98 %/167.5° C	97.5 %/170° C
Residue	1.0 %	1.0 %
Loss	1.0 T	1.5 %
10% by Vol.	71.5°	72.0°
90% by Vol.	145.0°	150.5°
100° Point.	47.5 Vol.%	45.0 Vol. %
Characterization Number*	105.2	107.6
Aniline Point °C	+ 16	+ 12
Corrosion Test	Negative	Negative
Doctor Test	"	"
Bomb Test - 0.12% by Vol. Pb		
Gum, mg/100 mls	9.5	9.5
Lead sludge, mg/200 mls	9.0	10.5
Iodine Number, Hanus	1.1	1.3
Hydrocarbons:		
% by Vol. Aromatics + Olefines	42	45
Naphthenes	37	35
Paraffins	21	20
Ultimate Analysis		
C	87.88 %	88.00 %
H	12.06 T	12.00 %
Octane Number (mot. meth.)		
Not leaded	77.5	78.0
+0.05% by Vol.	86.5	87.0
+0.12% by Vol.	90.0	90.0

*The "Characterization Number" is the average boiling point of a gasoline.

It is determined by adding the boiling points at 5, 15, 25...95% distillates and dividing the sum by 10. It is merely a measure of the volatility of the gasoline, and much importance is not attached to it in Germany. v. D. Holde, "Kohlenwasserstoffe und Fette", Berlin, 1933, p. 195. (Translator).

IV Analysis of Gaseous Products of the Reaction and the Computation of Gasification.

The C-numbers of the gasified hydrocarbons in the converter gas and the gaseous product were determined for computation of daily balance losses. In addition, the converter gas and the gaseous products in the principal phases of the test, as well as the gas dissolved at atmospheric pressure in the products of the different apparatus units were investigated, and the gasification based on these accurate analytical values.

The gasified hydrocarbons were calculated, and the amount of n butane, dissolved to a vapor pressure of 0.4 atm in gasoline (around 2% of the gasoline) was subtracted. The gasified hydrocarbons were referred to the gasoline obtained + gasification.

Following the example of the I. G. Ludwigshafen, the carbon content of the gasified hydrocarbons was calculated and referred to carbon in gasoline + carbon in the gas. In these computations, the n-butane remaining in solution in the gasoline was not taken into consideration.

Gas samples were taken for 16 hours on a day on which the stall was completely in equilibrium. The amounts of gas were referred to normal volumes (760 mm; 0° C), and the deviations from the gas laws were taken into account in the recalculation from % by volume to % by weight.

1. Test with Scholven-Gasoline-Containing Middle Oil at 25.5 mv.

Experimental Conditions:

Temperature	25.5 mv.
Pressure	500 atm.
Load	1.45 kg/li/hr
Tested on the	19-th day.

	Converter Gas % by Volume	Gas from Products % by Volume	Gas in Solution in the Product % by weight
Amount of Gas or of the Product	325.0 m^3	9.934 m^3	167.3 kg
CO_2	0.00	0.00	--
H_2S	0.00	0.13	--
O_2	0.00	0.00	--
H_2	95.52	63.05	--
CO	0.16	0.25	--
N_2	2.84	2.20	--

Total Gasification Referred to Injection

(injection = 184.6 kg)

	% by Wt. of Hydrocarbons	% by Weight of Carbon
CH_4	0.79	0.59
C_2H_6	1.20	0.96
C_3H_8	3.59	2.93
$i\text{-}C_4H_{10}$	1.32	1.09
$n\text{-}C_4H_{10}$	1.88	1.55
C_5H_{12}	3.62	Total 7.12

Obtained from 100 kg Injection:

a) in catchpot: 40.33 kg gasoline (C = 87.77%) = 35.59 kg C

b) in the gaseous product, pentane and higher hydrocarbons:

1.02 kg = 0.85 kg C

c) in the gasoline, additional 0.80 kg butane = 0.66 kg C

Total = 42.15 kg gasoline = 36.90 kg C

Remaining Gasified Hydrocarbons:

CH_4	0.79 % by wt.	
C_2H_6	1.20 " "	
C_3H_8	3.59 " "	
$i\text{-}C_4H_{10}$	1.32 " "	$i\text{-}C_4H_{10}$ in total C_4H_{10} = 55%
$n\text{-}C_4H_{10}$	1.08 " "	
Total	7.98 % by wt. to injection	

Gasified Hydrocarbons: gasoline + gasification = 15.9%

Gasified Carbon : Carbon in gasoline + gasified carbon = 16.4%

2. Test with Gasoline-Containing Scholven Middle Oil at 26.5 mv

Experimental Conditions:

Temperature	26.5 mv.
Pressure	540 atm.
Load	1.45 kg/li/hr
Tested on	41-st day

	Converter Gas % by Vol.	Gas Produced % by Vol.	Gas Dissolved in the Products % by Weight
Amount of Gas or of the Products	329.8 m^3	12.91 m^3	162.4 kg
CO_2	0.00	0.00	--
H_2S	0.00	0.10	--
O_2	0.00	0.00	--
H_2	94.55	55.94	--
CO	0.25	0.26	--
N_2	2.70	1.79	--
CH_4	1.20	3.12	0.00
C_2H_6	0.24	7.72	0.41
C_3H_8	0.87	13.19	0.60
$i\text{-}C_4H_{10}$	0.19	4.60	0.62
$n\text{-}C_4H_{10}$		7.06	1.81
C_5H_{12}	--	4.98	3.20
C_6H_{14}	--	1.24	--

Total Gasification to Injection (injection 184.1 kg)

	Hydrocarbons % by weight	Carbon % by weight
CH_4	1.70	1.27
C_2H_6	1.68	1.34
C_3H_8	5.53	4.52
$i-C_4H_{10}$	1.78	1.47
$n-C_4H_{10}$	3.48	2.87
C_5H_{12}	4.00	Total: 11.47

100 kg Injection Produced:

a) from the catchpot: 47.26 kg. gasoline (C = 87.87%) = 41.51 kg.C.

b) C_5H_{12} and higher hydrocarbons in the products --1.52 kg =1.27 kg C

c) 0.95 kg n-butane = 0.78 kg C are obtained in addition from gasoline.

Total: 49.73 kg gasoline = 43.36 kg C

Hydrocarbons Still Remaining Gasified:

CH_4	1.70 %	
C_2H_6	1.68 %	
C_3H_8	5.53	
$i-C_4H_{10}$	1.78	$i-C_4H_{10}$ in total C_4H_{10} = 41.%
$n-C_4H_{10}$	2.53	
	13.22 % of the injection	

Gasified hydrocarbons to Gasoline + Gasification = 21.0 %

Gasified carbon to carbon in Gasoline + carbon in gasified hydrocarbons 21.1%

3. Test with Gasoline-Free Scholven Middle Oil at 26.5 mv.

Experimental Conditions:

Temperature	26.5 mv
Pressure	540 atm.
Load	1.0 kg/li/hr
Test on	56-th day

	Converter Gas % by Vol.	Gas Produced % by Vol.	Gas Dissolved in Product % by weight
Amount of Gas or Product	315.7 m^3	8.31 m^3	108.2 kg
CO_2	0.00	0.00	--
H_2S	0.09	0.06	--
O_2	0.00	0.00	--
H_2	95.84	56.65	--
CO	0.23	0.21	--
N_2	2.04	1.60	--
CH_4	0.73	2.45	0.01
C_2H_6	0.16	6.28	0.05
C_3H_8	1.00	13.27	0.63
i-C_4H_{10}	--	4.92	0.73
n-C_4H_{10}	--	8.50	1.84
C_5H_{12}	---	3.45	5.65
C_6H_{14}	--	2.60	--

Total Gasification to Injection (125.0 kg injection)

	% by Wt. of Hydrocarbons	% by Wt. of Carbon
CH_4	1.44	1.08
C_2H_6	1.16	0.92
C_3H_8	7.41	6.06
$i\text{-}C_4H_{10}$	1.50	1.24
$n\text{-}C_4H_{10}$	3.12	2.58
C_5H_{12}	5.66	11.88

Obtained, per 100 kg injection:

a) from catchpot: 48.25 kg. gasoline ($C = 87.98$) = 42.45 kg C

b) n-butane may be absorbed by the gasoline: 0.97 kg = 0.80 kg C

Total: 50.68 kg gasoline = 44.47 kg C

The remaining gasified hydrocarbons are:

CH_4	1.44 % by Wt.	
C_2H_6	1.16 " "	
C_3H_8	7.41 " "	
$i\text{-}C_4H_{10}$	1.50 " "	$\frac{i\text{-}C_4H_{10}}{C_4H_{10}}$ in total = 41.0 %
$n\text{-}C_4H_{10}$	2.15 " "	
Total	13.66 % by weight to injection	

Gasified hydrocarbons to gasoline + gasification = 21.2 %

Gasified carbon to carbon in gasoline + C in gasification = 21.4 %

4. Test with Gasoline-Free Upper Silesian Middle Oil

Experimental Conditions:

Temperature	26.5 mv
Pressure	550 atm.
Thruput	1.1 kg/li/hr
Tested on	60-th day

	Converter Gas % by Vol.	Gas Produced % by Vol.	Gas Dissolved in product % by weight
Amount of Gas or Products	231.6 m^3	10.13 m^3	122.0 kg
CO_2	0.00	0.00	--
H_2S	0.00	0.02	--
O_2	0.00	0.00	--
H_2	95.45	54.81	--
CO	0.35	0.16	--
N_2	2.18	1.70	--
CH_4	0.79	2.56	0.00
C_2H_6	0.20	7.29	0.06
C_3H_8	1.03	14.15	0.65
$i\text{-}C_4H_{10}$	--	4.86	0.75
$n\text{-}C_4H_{10}$	--	8.63	1.81
C_5H_{12}	--	3.92	4.53
C_6H_{14}	--	1.91	--

Total Gasification to Injection (144 kg injected)

	Hydrocarbons % by Wt.	Carbon % by Wt.
CH_4	1.42	1.06
C_2H_6	1.37	1.09
C_3H_8	7.34	6.00
$i\text{-}C_4H_{10}$	1.54	1.27
$n\text{-}C_4H_{10}$	3.18	2.63
	Total	12.05
C_5H_{12}	4.76	

Obtained from 100 kg. injection:

a) in the catchpot: 44.30 kg gasoline (C = 87.44) = 38.75 kg C

b) C_5H_{12} and higher hydrocarbons in the gaseous product = 1.46 kg = 1.22 kg C

c) n-butane which may be absorbed in gasoline = 0.89 kg = 0.74 kg C

Total: 46.65 kg gasoline = 40.71 kg C

Hydrocarbons remaining Gasified:

CH_4	1.42 % by wt.	
C_2H_6	1.37 "	
C_3H_8	7.34 "	
$i\text{-}C_4H_{10}$	1.54 "	$i\text{-}C_4H_{10}$ in total C_4H_{10} = 40 %
$n\text{-}C_5H_{12}$	2.29 "	
Total	13.96 T by wt. of injection	

Gasified hydrocarbons, to gasoline + gasification = 23.0 %

Gasified carbon, to carbon in gasoline + gasified carbon = 23.2 %

V. Summary

1. From Scholven gasoline-containing coal liquefaction oils, under 500 - 540 at pressure and with a load of 1.45 kg/li/hr, the yield was:

at 25.5 mv - 0.58 kg/li/hr

at 26.0 mv - 0.65 kg/li/hr

at 26.5 mv - 0.68 kg/li/hr

From Scholven gasoline-free middle oil, with 550 atm. pressure, at 26.5 mv and a thruput of 1.0 kg/li/hr, the yield was 0.48 kg/li/hr; it was still 0.41 kg/li/hr with a pressure of 450 atm.

Using Upper Silesian coal liquefaction oil under 550 atm, at 26.5 mv and a thruput of 1.3 and 1.0 kg/li/hr, the yield was gasoline-containing middle oil 0.70 kg/li/hr; with gasoline-free middle oil --- 0.52 kg/li/hr. These yields remained constant over longer test periods. No loss in efficiency of the catalyst has been observed.

2. Scholven gasoline-containing middle oil under 540 atm. at 26.5 mv and with a thruput of 1.45 kg/li/hr produced gasoline with 42% aromatics. This gasoline, with a boiling point up to 165° C still had 49% by vol. of a fraction boiling below 100°. The octane number of this gasoline (motor method) was 78.0. With the addition of 0.05% by vol. of lead, the octane number was raised to 87.0.

The gasoline obtained from the gasoline-free Scholven oil (550 atm, 26.5 mv, thruput of 1.0 kg/li/hr) contained 45 aromatics. 48% of the gasoline distilled below 100°. The octane number of the gasoline was 79.0, with 0.05 % by vol. of lead - 85.5 to 97.5. The gasolines are being tested by the D.V.L. in overload motors.

3. The gasolines can be readily refined and produces then an aviation gasoline which satisfies all requirements.

4. With gasoline-containing Scholven middle oil, gasification losses at 25.5 mv were equal to 16% (to gasoline + gasification), at 26.5 mv --- 21 %.

With gasoline-free Scholven middle oils the gasification at 26.5 mv was also 21 %.

The gasification with gasoline-free Upper Silesian oil was 23%.

A comparison of gasification losses were found in pilot plants with those in a large scale production show the former to be always about 2% higher.

5. The proportion of isobutane in the total butane was around 40% at 26.5 mv, with any of the raw materials studied. It is higher at lower temperatures (at 25.5 mv, it is equal to 55%).

/s/ Ibing

W. M. Sternberg

TOM Reel 174
Pp. 481-525

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

T-218

KCBraun
1-24-47

DEVELOPMENT OF THE METHANOL SYNTHESIS AND OF CATALYTIC PRESSURE HYDROGENATION TO DATE

Report on Lecture by Dr. M. Pier, October 28, 1942.
(Abridged.)

Before the first world war, Dr. Pier conducted high pressure experiments on CO-H_2 reactions in the Nernst laboratory. Then, in 1923, he succeeded in the high pressure methanol synthesis in the laboratory of the Badische Anilin & Soda Fabrik at Ludwigshafen. A practical, quantitative conversion of water gas to methanol was obtained with the aid of catalysts at a temperature of about 400° C and pressure of, first, 1000 and then 200 atm. Within a period of 6 months the process was applied on an industrial scale at Leuna. The isobutyl synthesis was also discovered at the same time. An extensive development of synthetics, fuels, cleansers, solvents and other important products of organic chemistry followed, based on the two syntheses.

The successful high pressure hydrogenation of coal and oil to gasoline, with poison-proof catalysts, closely followed the methanol synthesis. The basic experiment with a sulfur-proof Mo-catalyst, which yielded 1 part/vol. gasoline from 1 part/vol. brown coal tar, succeeded in January 1925. It was soon realized that the process had to be subdivided into 2 stages, ~~the liquid and the vapor phases, in order to obtain greater~~ catalyst effectiveness and greater thruput.

Based on small, continuous experiments, it was decided to build a larger experimental plant of 100,000 t/ann. at Leuna, which started operations in April 1927. So many difficulties in heating and heat exchange, construction materials, etc. particularly in the liquid phase and residue processing, were encountered that in 1929 to 1932 it was decided to convert operations from direct hydrogenation of coal to the hydrogenation of tars and oils. In 1932, however, the problem of direct hydrogenation of coal was solved by increased decomposition and consequent decreased residue processing and direct hydrogenation of coal was successfully resumed. In 1933 the production was increased to 300,000 t/ann, which was again doubled in 1940. This was done without building any new stalls and the originally calculated production costs were realized.

By 1934 the hydrogenation of bituminous coal had also been developed. In order to increase the sources of raw materials and to perfect the processing of asphalt, the 700 atm. liquid phase hydrogenation was developed. Besides gasoline, diesel oil, lubricating oil and paraffin are produced, particularly in brown coal and brown coal tar plants, and fuel oil, particularly in plants processing bituminous coal and pitch.

In competition with the Fischer process, coal extraction, etc., hydrogenation has formed the broad basis of German motor fuel supply, in particular for practically all aviation gasoline.

The development of German aviation gasoline production generally diverged from the course followed by other countries with more abundant oil supplies. Iso-octane is synthetically produced from CO-H_2-isobutyl oil and is also obtained from hydrogenation off-gases, just as alkyloctane. However, most of the high grade fuels today are gasolines rich in aromatics, produced by the DHD process.

The DHD process produces products particularly rich in aromatics, from which toluol, e.g. can be obtained. It is possible to produce considerably more toluol by bituminous coal hydrogenation than by coking. Phenols can be obtained from the products of hydrogenation in a similar manner.

An indication of the importance of bituminous coal hydrogenation as a basis for raw materials for the chemical industry are the solid, pure aromatics produced in the decomposition of coal. The solid aromatics are characterized by their symmetrical structure, as pyrenes, corones, carbazol and benzperylene.

With the exception of Pölitz, I.G's. motor fuel production is based on brown coal and its proportion of the total motor fuel production is comparatively small. It has been repeatedly pointed out since 1933 that bituminous coal is of greater interest to chemistry than brown coal or petroleum. It has also been shown at Leuna that the chemical products produced from brown coal besides gasoline are steadily increasing in value. The production costs of processing bituminous coal at Hydrogenation Works Scholven have turned out to be very satisfactory, even without a nitrogen plant in connection with it. The utilization by the chemical industry of the chemical by-products of bituminous coal hydrogenation is of the greatest importance today.

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Change in Hydrogen Content by Liquid and Vapor Phase Hydrogenation.

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

Hydrogen Consumption

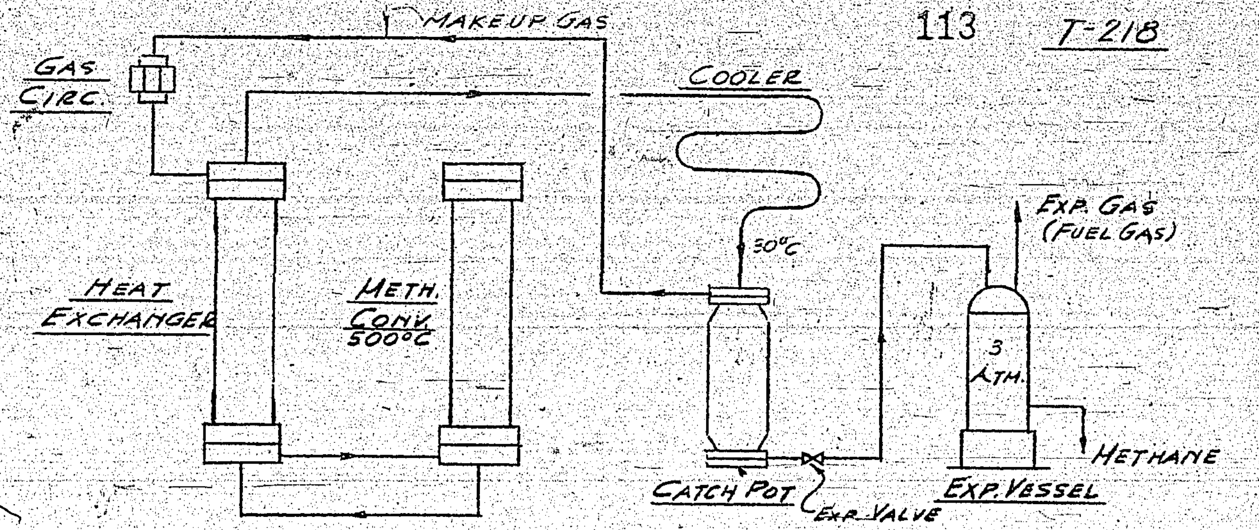
Raw Material	End Product	Chem. H_2/t End Product
Bitum. Coal	Auto Gasoline	2800
Brown Coal	" "	2400
Coke Oven Tar	" "	2100
Bitum. Coal Crude Tar	" "	1300
Brown Coal L.T.C. Tar	" "	850
Petroleum Residue	" "	900
Gas Oil	" "	500
Bitum. Coal	Fuel Oil and Auto Gasoline	2100
Brown Coal	Diesel Oil	1900
Petroleum Residue	" "	500
Brown Coal L.T.C. Tar	TTH-Diesel Oil, Lubricat. Oil, Paraffin.	550

Requirements of Mo and W in Catalysts for the Production of Gasoline

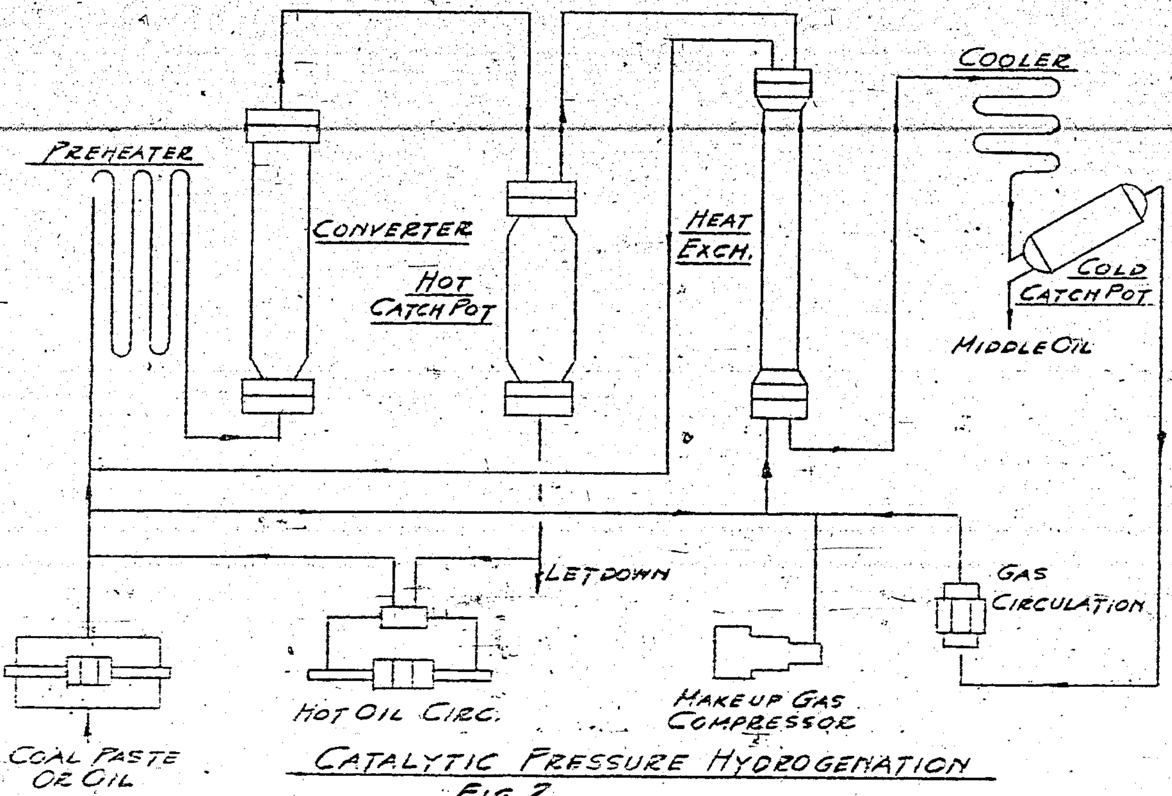
Catalyst	kg W or Mo Per m^3 Catalyst.	Catalyst Combination for Vapor Phase Hydrogenation.	Tons W or Mo per 100,000 t/ann Aviation Gasol.
5058	2000 W	5058/5058	83
6434	70 W	5058/6434	32
7846 W	200 W	5058-7846 W/6434	14
		7846 W/6434	4.3
7846	70 Mo	7846/6434	2.1

PRODUCTION OF AVIATION GASOLINE BY VARIOUS PROCESSES

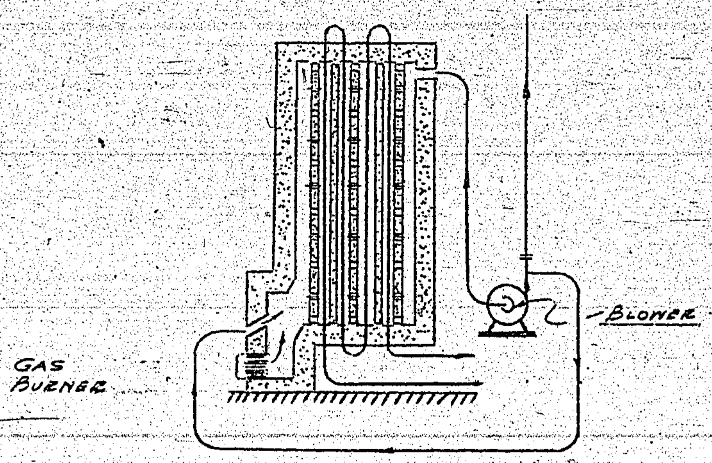
	Hydrogenation			DHD	Cracking		Combination
	Benzination	Aromatization.	Middle Oil Splitting		Catalytic	Thermal	Cat. Crack. + Benzin.-?
Feed Stock	Mi-Oil	Mi-Oil	Mi-Oil	Gasoline	Mi-Oil	Mi-Oil	Mi-Oil
Origin	Coal	Coal	Oil, Hydr. Prod.	Optional	Oil, Hydr. Prod.	Oil, Hydr. Prod.	Coal, Oil, Hydr. Prod.
Temperature, °C	400	500	500	520	420	480	
H_2-Pressure	0-600	180-600	25-70	5-25	0	0	
Catalyst	6. Group Carrier	6. Group Carrier	6. Group Al_2O_3	6. Group Al_2O_3	Hydro-Silicate	--	
Life of Catalyst	1 year +	1 year +	25 hrs. +	8 hrs. +	?	--	
Aviat. Gasoline Produced:							
Yield, %/Wt.	80	75	70	75-90	22	50	75
Aromatics, %/Vol.	5	30-50	20	50	15	20	10
Motor Octane No.	72	76-80	74	80	76	70 No Aviat. Gasol.	75
" " " + 0.2% tet-eth-ld	90	90	88	92	92	86	91



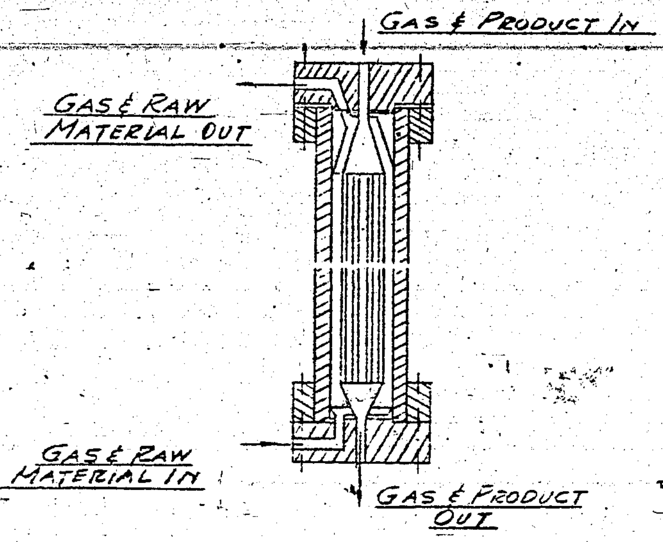
METHANE SYNTHESIS
FIG. 1



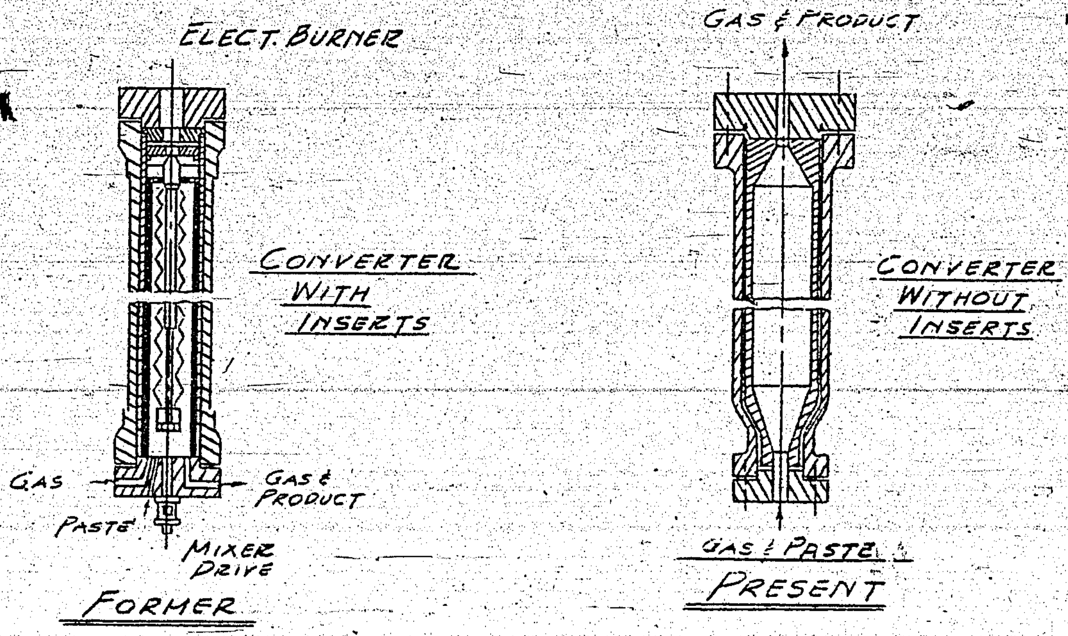
CATALYTIC PRESSURE HYDROGENATION
FIG. 2



GASFIRED PREHEATER
(1942)
FIG. 3

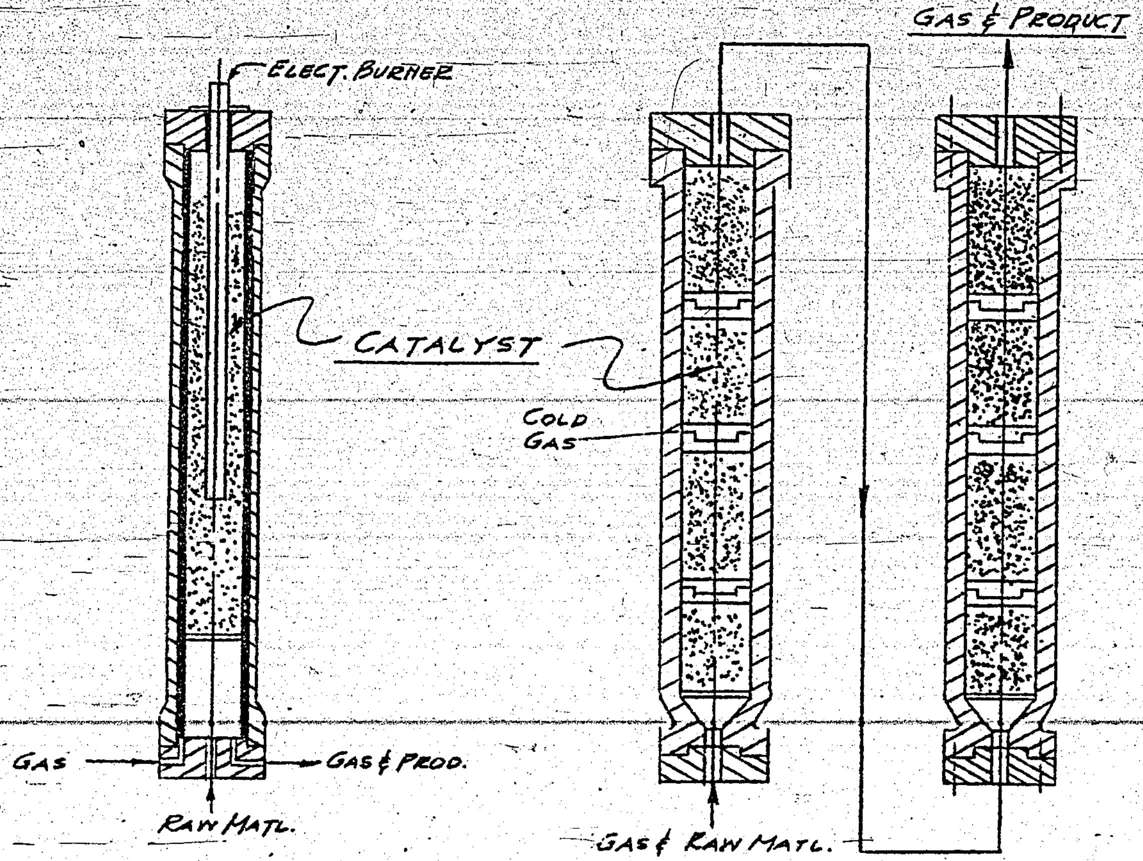


·HEAT EXCHANGER
(1942)
FIG. 4



DEVELOPMENT OF THE LIQUID PHASE CONVERTER (1941)

FIG. 5

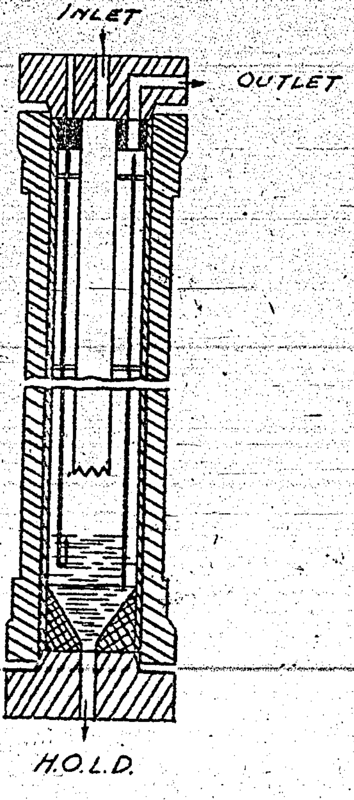


FORMER

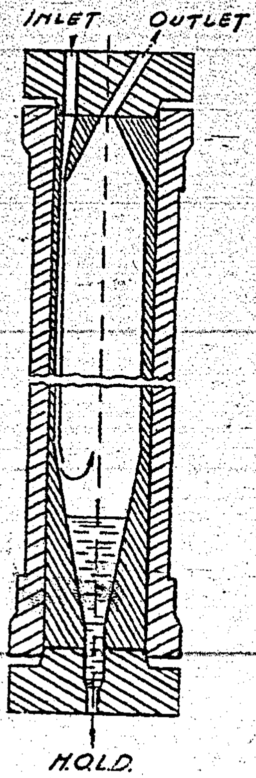
PRESENT

DEVELOPMENT OF THE VAPOR PHASE CONVERTER (1942)

FIG. 6



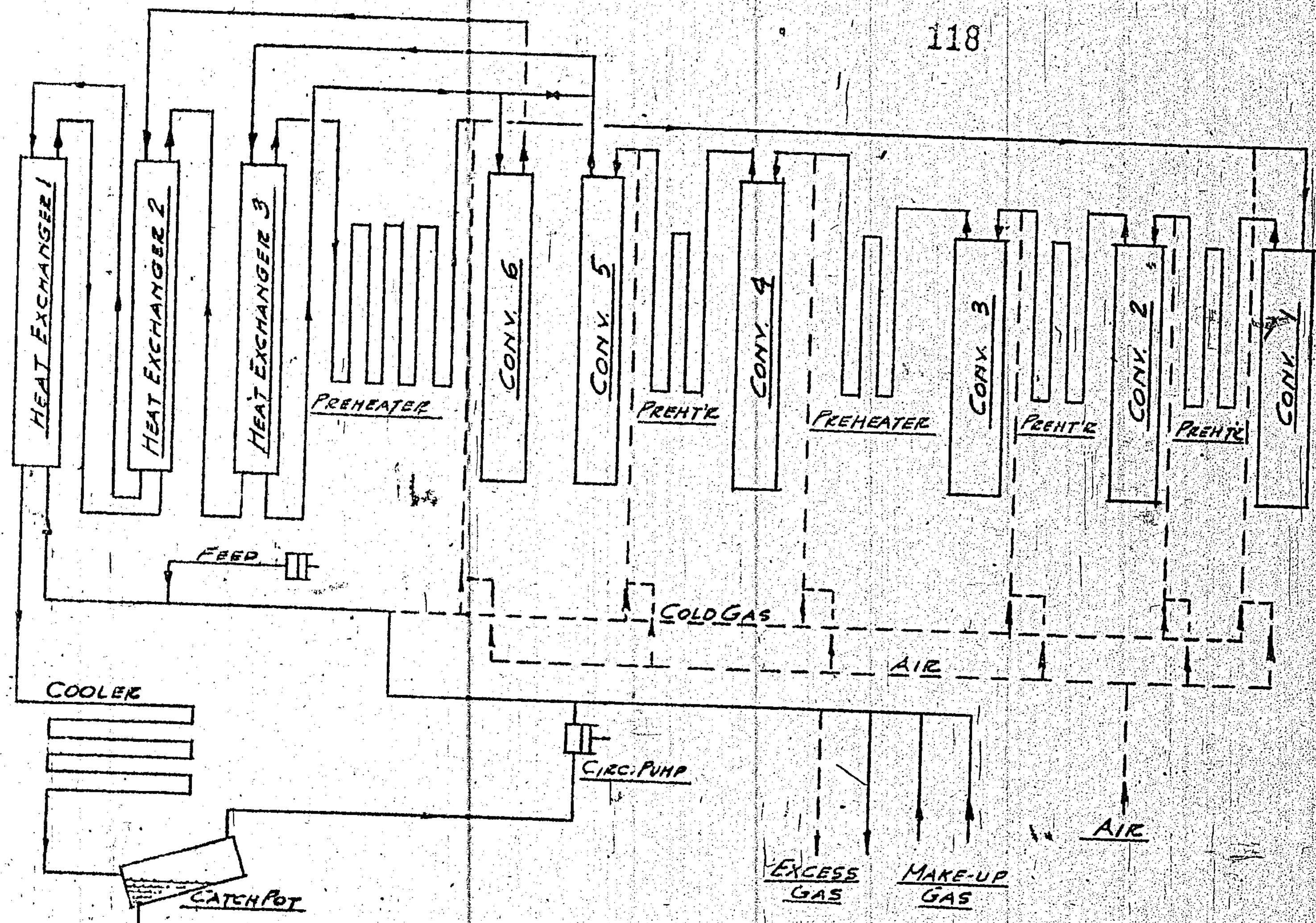
FORMER



PRESENT

DEVELOPMENT OF THE HOT CATCH POT
(1942)

FIG. 7



DHD Unit Stall
(1941)

Fig. 8

AROMATICS FROM 1000 KG. BITUM. COAL
(LOW MOLECULAR AROMATICS)

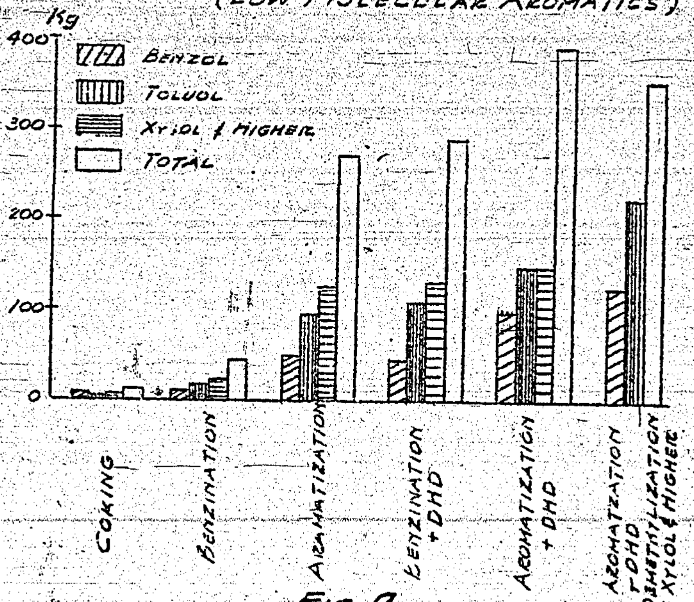


FIG. 9

PHENOLS FROM 1000 KG BITUM. COAL
(FREE OF ASH & WATER)

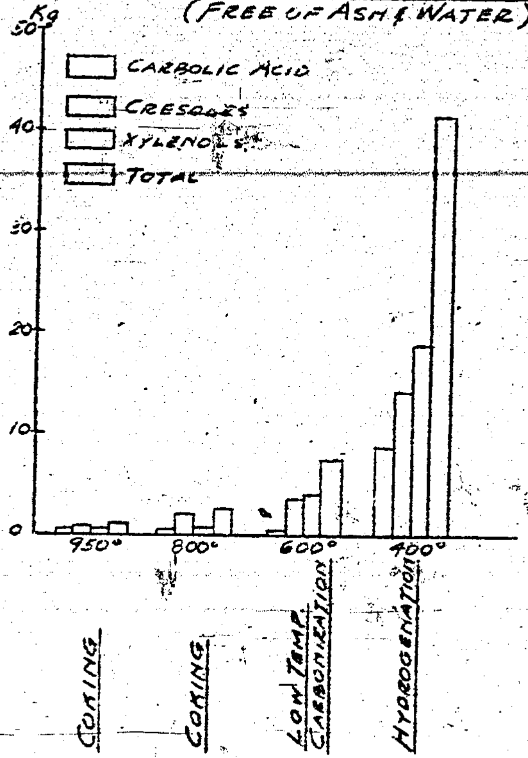
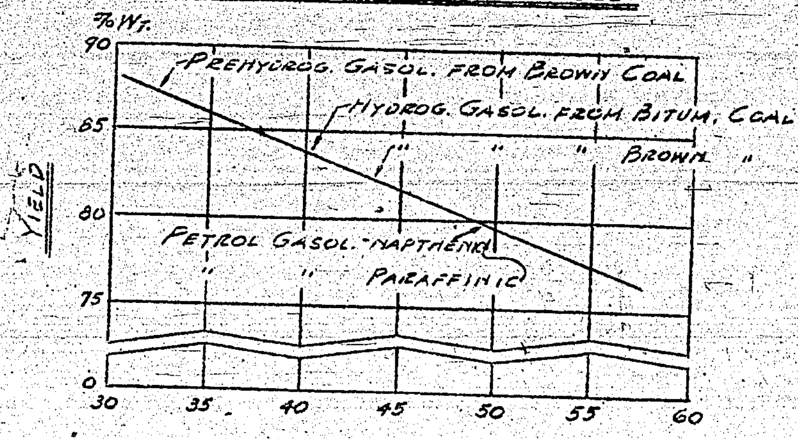


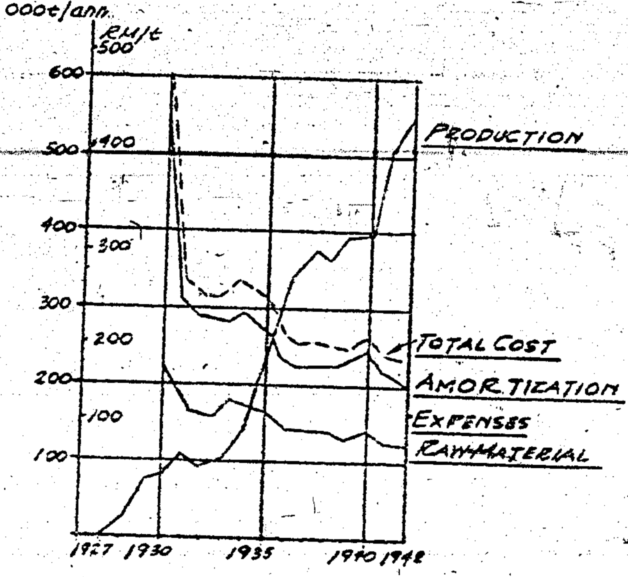
FIG. 10



YIELD WITH DHD PROCESS

ANILINE POINT OF THE HEAVY GASOLINE FRACTION OF THE FEED GASOLINE

FIG. 11



LEUNA PRODUCTION & COSTS

FIG. 12

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

121

T-219

KCBraun
1-24-47

THE RECOVERY OF BY-PRODUCTS IN HYDROGENATION

By Dr. Frese, Jan. 24, 1947

The principal product of high pressure hydrogenation from bituminous coal is gasoline with a high octane number. However, many by-products may be obtained, which are considerably higher in price and whose recovery will greatly increase the efficiency of hydrogenation. Attempts have been made in Germany in recent years to recover these by-products, but we are convinced that these attempts represent only a modest beginning and that the products of bituminous coal hydrogenation in the middle or upper boiling range, with their strongly aromatic or hydro-aromatic character, will form the basis of compounds destined to play an important role in this or that industry.

The attached diagram shows the proportion of known by-products from 100 kg of dry coal free of ash, for which a demand exists in industry and which, in part, are also obtained in Germany. Of course, these products are dependent upon the kind of coal processed and the method of operation. The figures given in the diagram must, therefore, be considered only approximations indicating the trend.

Of the known by-products from 100 kg. of dry and ash-free coal the following are obtained:

1). 1 to 2 kg. of pyrenes, corones, carbazol and similar higher organic compounds, which are of importance partly for the production of dyes and partly for the production of luminescent and phosphorescent substances. These substances have, in part, been difficult to obtain in the past and it is quite possible that an increased field of application will be found for them with increased production.

These products have been mainly found in the upper boiling range of the liquid phase catch pot, but were also present in the let-down. Their recovery from the let-down rich in asphalt is very difficult and questionable. For the recovery of these products we would recommend the insertion of a second catch pot behind the first hot catch pot, in which a small part of the catch pot product, which would probably contain the greater portion of these products in concentrated form, will be precipitated free of asphalt by cooling or the addition of wash oil. The complete precipitation would have to be done by the addition of low boiling products. Recovery could then be effected by subsequent centrifuging. To separate the individual products, subsequent vacuum distillation, fractionating cristallization, or other measures, would be required.

The presence of these products showed itself in various plants by precipitations and clogging in the catch pot cooler or in the distillation lines. It would, therefore, be desirable to remove them before in the manner described above.

With the liquid phase and vapor phase arranged in series without intermediate de-compression, the second catch pot would also represent an additional safety measure against the carryover of asphalt onto the vapor phase catalyst.

2). About 5 kg, phenols, depending upon the O_2-content of the feed coal, are present in the liquid phase catch pot, but only in the fraction boiling between 180-220°C. About 30% of these phenols consists of carbolic acid, the rest of cresols and xylenols. These products form the raw materials for the production of synthetic resins, disinfectants and other substances. The mixture of cresol and xylenol, after the removal of the carbolic acid and in the form in which it is obtained, has been found to be an excellent stabilizer (inhibitor) for leaded gasolines. All German aviation gasolines produced in Welheim during the late war years were stabilized with 0.01% of this inhibitor.

The recovery of these products would properly be effected from a fraction boiling between 180-220°C taken off in the A-distillation.

Of course, if the liquid and vapor phase stalls were arranged in series without intermediate expansion, the phenols would be largely reduced with the catalysts in use today. Catalysts would then have to be developed, which, at least, would not attack the greater portion of the phenols.

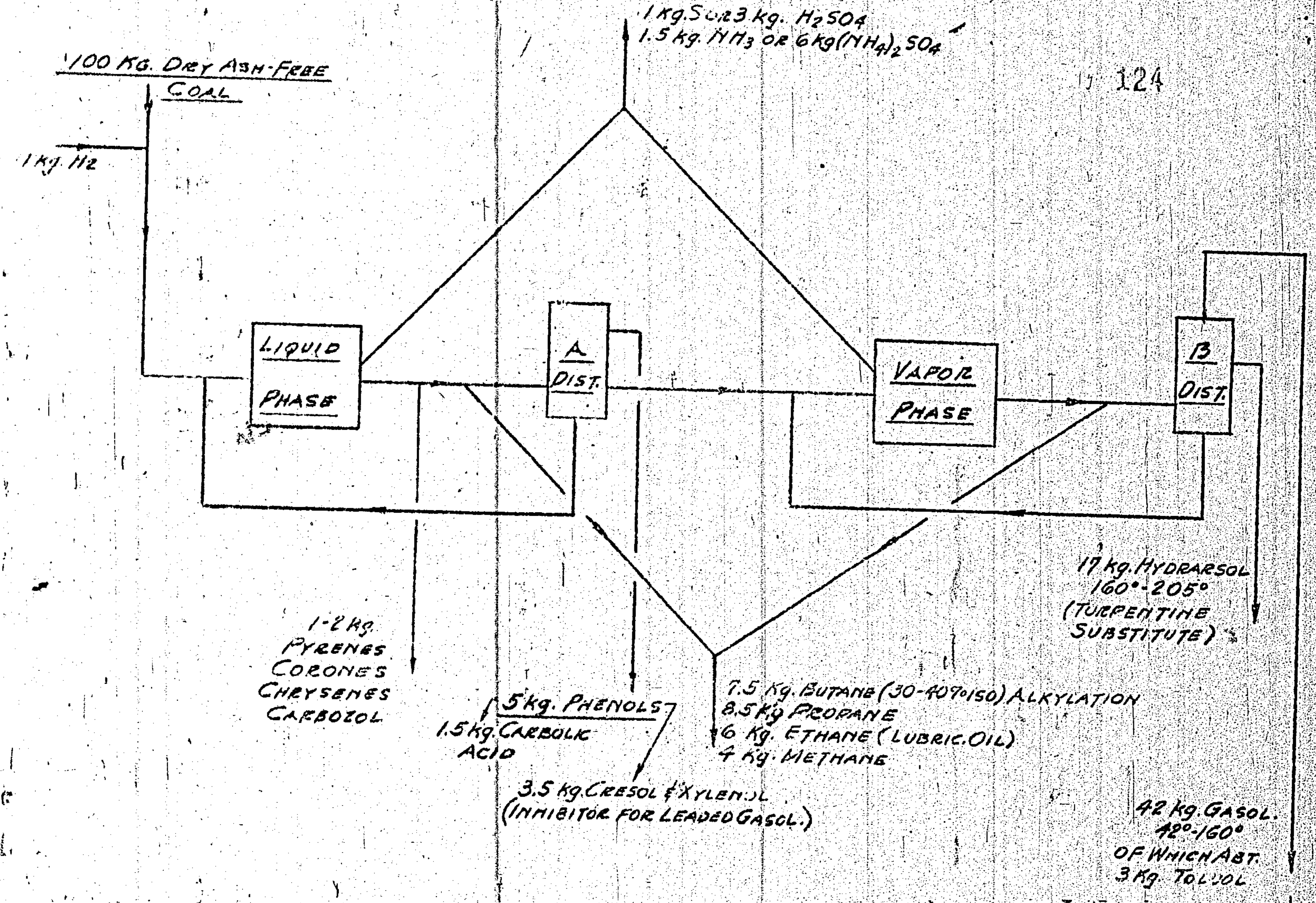
Carbolic acid is the most difficult to reduce of all the phenols. It would accordingly, remain to the last. In general, carbolic acid commands the highest price of the common phenols.

3). If the catalyst is correctly chosen, the entire fraction of the vapor phase catch pot boiling between about 160-205° may be recovered as a product clear as water and very similar in its chemical characteristics to oil of turpentine, including its specific gravity. The demand for suitable solvents in the entire chemical solvents industry, particularly in the paint and varnish field, is very great and further increases in demand must be counted on. Experiments in Germany in recent years with this product clearly indicated the superiority of this hydrogenation product, called "Hydrarsol" (Hydr. + aromatic + solvent), over oil of turpentine in the field of lacquer production. The quantity obtained is relatively high and equals about 17 kg.

4). About 3 kg. (7%) toluol may be recovered from the gasoline, depending upon whether the cresols are removed before or carried over to the vapor phase for reduction.

5). About 7.5 kg. butane, 8.5 kg. propane, 6 kg. ethane and 4 kg. methane are obtained in off-gases. Iso-octane can be made from the butane by alkylation, which increases the proportion of gasoline. Valuable lubricating oils can be made from the ethane by way of ethyline and subsequent condensation.

6). About 1% sulfur (3½% H_2SO_4) or 1.5% NH_3 (6% ammonium-sulfate) can be recovered from the sulfur and nitrogen constituents of the coal. Assuming that America's entire gasoline requirement were derived from coal, the entire world demand for nitrogen and sulfur could probably be covered from these by-products.



PRODUCTS OF HYDROGENATION

T-219

TOM Reel 57
Pp. 748-776

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

T-220

KCBraun
1-28-47

AROMATIC MOTOR FUELS

By Dr. Mathias Pier. (Abridged).

General Anti-Knock Characteristics of Hydrocarbons.

The motor fuels used in practice are mixtures of hydrocarbons of varying molecular weight and constitution. To obtain high anti-knock motor fuels, each individual constituent of the hydrocarbon mixture must have as high an anti-knock value as possible.

Fig. 1. shows the relation between the anti-knock value of various hydrocarbons and their boiling point, i.e. their molecular weight.

It may be observed that the anti-knock value of the normal paraffins drops sharply with rising boiling point, i.e. with a long straight chain, and reaches 0 with n-heptane, boiling point 98°C. With the naphthenes also, the octane number drops with rising boiling point, as shown for the 5-ring naphthene. The 6-ring naphthenes have a somewhat higher octane number, though similarly dependent upon the boiling point. The unsaturated show a similar behavior, though their anti-knock value increases if the double combination is shifted towards the center of the molecule. Even though the unsaturated are, generally speaking, not likely to be considered as aviation gasoline, because of their poor storage properties and tendency to pitch formation, the olefins recently produced by catalytic cracking, mono-olefins not too highly concentrated, form an exception. Contrary to the straight chained paraffins, the strongly ramified isoparaffins show very good anti-knock values, even in the higher boiling range. For instance, iso-octane (2.24-trimethylpentane) by definition has an octane number of 100, while the n-octane has an octane number of only 20. The aromatics have still higher octane numbers than iso-octane, their anti-knock value even rises at first with rising boiling point.

The physical data of a few important isoparaffins may be seen in Table 1. Among the isoparaffins, particular attention is called to the 2.2.4-trimethylbutane, the socalled "triptane", with which an appreciably greater performance was obtained than with iso-octane, according to American reports. Increased interest is also being accorded "neohexane", the 2.2-dimethylbutane, because it boils below iso-octane and has an especially high lead sensitivity. It can, therefore, be mixed with 100 octane motor fuels containing iso-octane. For isoparaffins, in general, the anti-knock value increases with increased ramification and symmetrical arrangement of the side chains.

Table 1, Physical Data of Isoparaffins.

	Formula	Boiling Point °C	Melting Point °C	Spec, Gravity @ 20° C	Mol Wt.	H_2-Content %/wt.	Heat Value, Hu		Mot.-Meth. Mixture Octane No.
							kcal/kg.	kcal/Lit.	
Iso-pentane	C_5H_{12}	28	-24	0.620	72.0	16.6	10650	6600	90
Neo-hexane	C_6H_{14}	50	-100.1	0.649	86.1	16.3	10600	6900	105
Triptane	C_7H_{16}	81	-25	0.686	100.1	16.0	10550	7240	125
Iso-octane	C_8H_{18}	99	-107.4	0.692	114.1	15.8	10500	7260	100
Iso-dodecane	$C_{12}H_{20}$	193	--	0.737	170.2	15.3	10500	7750	93

The use of isoparaffins for the production of anti-knock aviation gasolines is logical in countries having plenty of petroleum. Their production requires unsaturated hydrocarbons and a large production is, therefore, dependent upon an extensive cracking industry. In the U.S.A. a small part of the available cracking gases would be sufficient to cover the entire present demand for high performance motor fuels. Conditions in Germany are entirely different. We have a highly developed motor fuel industry based on catalytic pressure hydrogenation and CO-H_2-synthesis, the first of which is of primary importance for the production of high performance motor fuels. However, the gases produced herewith do not form a sufficient basis for the production of high performance motor fuels based on iso-paraffin. The iso-octane synthesis from CO and H_2 by way of isobutyl oil was, therefore, developed. Above all, however, comparatively simple aromatic hydrocarbons can be produced by pressure hydrogenation, for which reason we in Germany are dependent upon aromatics for high performance fuels.

Characteristics of Aromatics, Particularly Their Behavior in the Motor

The basic type of aromatic is benzol, which, after thorough refining, is used as aviation benzol together with small quantities of toluol and xylol mixed with aviation gasoline. Table 2 shows the physical data of a number of important pure aromatics. Besides their high octane number, they are superior to isoparaffins in their appreciably higher heat value per liter. This ~~is of importance, because in many modern airplanes the question~~ of space is more important than that of weight. The disadvantage of benzol, that it solidifies at low temperatures, is eliminated in the higher aromatics because their melting point is generally far below 0°C.

The octane numbers (motor method) given in the Table are mixture octane numbers. These are determined by mixing the substance to be tested with a gasoline of known octane number and then calculating the anti-knock value from the octane number obtained for the mixture by the mixture rule.

The determination of the mixture octane number is important, on the one hand, because the anti-knock value of hydrocarbons with very high octane numbers can no longer be determined, they can not be made to knock in the usual test motors. On the other hand, the mixture octane number gives us a picture

Table 2. Physical Data of Aromatics

	Formula	Boiling Point °C	Melting Point °C	Spec. Gravity @ 20° C	Mol. Wt.	H_2-Content %/wt.	Heat Value, Hu		M-M Mixture Octane No.
							Kcal/Kg	Kcal/Lt.	
Benzol	C_6H_6	80.4	+6	0.879	78.05	7.3	9630	8450	98
Toluol	C_7H_8	110.3	-14	0.867	92.06	8.7	9750	8450	98
o-Xylol	C_8H_{10}	144	-27	0.881	106.08	9.5	9825	8650	95
m-Xylol	C_8H_{10}	139	-54	0.864	106.08	9.5	9750	8420	100
p-Xylol	C_8H_{10}	138	+15	0.861	106.08	9.5	9780	8420	101
Ethyl benzol	C_8H_{10}	136	-94	0.867	106.08	9.5	9770	8460	100
1.3.5-tri-methyl benzol	C_9H_{12}	165	-46	0.865	120.1	10.0	9800	8460	109
1.4-ethyl-methyl benzol	C_9H_{12}	162	-20	0.862	120.1	10.0	--	--	110
n-propyl benzol	C_9H_{12}	159	-99.2	0.862	120.1	10.0	9890	8500	101
n-butyl benzol	$C_{10}H_{14}$	183	-81.2	0.861	134.1	10.5	---	--	99
1.4-Diethyl benzol	$C_{10}H_{14}$	183	-35	0.865	134.1	10.5	9858	8550	116
1.4-ethyl-isopropyl benzol	$C_{11}H_{16}$	193	-20	0.858	148.2	10.8	9945	8540	120

of the behavior of hydrocarbons in mixtures, which is of particular importance for hydrocarbons with narrow boiling range.

The value of the octane number very much depends upon the base gasoline and the concentration in the mixture of the motor fuel to be tested. The lower the octane number of the base gasoline the higher the mixture octane number of the substance to be tested, generally speaking, for all classes of hydrocarbons. For example, ethylpropyl-benzol in a 50%/vol. mixture with a base gasoline with an octane number of 40, has a mixture octane number of 117, while when mixed with a base gasoline with an octane number of 72 the mixture octane number is about 100.

The dependence of the mixture octane number on the concentration is not so simple. While, in general, the mixture octane number of isoparaffins is independent of it, it decreases sharply with increasing concentration in the unsaturated. Examples of the reverse effect can be found among the aromatics. For example, pure benzol mixed with paraffinic gasoline with an octane number of 42 shows an increasing mixture octane number from about 80 to 110. On the contrary, other aromatic hydrocarbons, as, for example, diethyl-benzol and ethylpropyl-benzol, show decreasing octane numbers with increased concentration. It is also possible that the formation of a mixture in the carburetor is strongly influenced by the high boiling range of these hydrocarbons at high concentration. A test in an injection motor would give a more accurate picture.

Because of their dependence on various factors, the mixture octane numbers must be evaluated with caution. However, they permit a valuable evalution of the anti-knock value in systematic tests, particularly with the new high anti-knock aromatic hydrocarbons.

While according to the motor method aromatics appear only about as knock-proof as iso-octane, they are uniformly better according to the research method, which also corresponds to results in practice. The reason for this discrepancy is in the different behavior of hydrocarbons towards changes in motor temperatures. Isoparaffins do not show any change in octane number with a rise in temperature, while aromatics show a more or less sharp drop. With the hydrocarbons investigated a decrease in temperature sensitivity was observed with rising boiling point.

Besides the temperature sensitivity, the sensitivity to tetraethyl-lead additions is also of importance in aviation gasolines. It has been shown that with rising aromatic content the temperature sensitivity generally increases while the lead sensitivity decreases. However, in anti-knock tests by the more practical overload process motor fuels with high aromatic content showed a good lead sensitivity.

The octane number is known to be a measure of how far the density ratio of the test motor can be increased before a knock appears. It is much dependent upon operating conditions and the construction of the motor. The introduction of overload motors, which require fuels with an octane number of 87, 100 and more, however, showed that the octane number evaluation was no longer adequate for aviation gasolines. For this reason, new test conditions were introduced which more closely fitted the test conditions to the modern airplane engine (overloading with a blower, pump injection of fuel) and regulates the knocking by increased load pressure rather than by increasing the density of the fuel.

The introduction of this new method showed that aromatic motor fuels were under-rated in their anti-knock qualities by the CFR motor method. If, for example, we take 2 gasolines with the same octane number, one with high isoparaffin and the other with high aromatic content, the aromatic gasoline may be far superior in an overload test. Aromatic gasolines are particularly superior in anti-knock qualities to isoparaffinic gasolines in an overload test of dense mixtures (excess air coeff. less than 1). With lean mixtures the overload capacity of aromatic fuels drops more rapidly, which runs parallel to their dependence upon temperature. But, in spite of this, aromatic fuels are superior in anti-knock qualities to isoparaffinic fuels of the same octane number in overload tests at load air temperatures of about 80° C, even with lean mixtures (excess air coeff. greater than 1).

Table 3 gives a summary of the results that may be obtained with various aromatic fuels by overloading, compared to known aviation fuels, in which the performance of a mixture of 50-50%/vol. of ethylpropyl-benzol and hydrogenation gasoline from bituminous coal with an addition of 0.12% lead at an excess air coefficient $\lambda = 0.9$ is set at 100.

Table 3

Overload Performance of Aromatic Motor Fuels

50%/Vol. Mixture of Hydrog. gasol. fr. bit. coal, octane number 73, + 0.12%/vol. Pb	% Performance @ Excess Air Coeff.		Octane Number	
	λ = 0.9	λ = 1.1	Motor Method	Research Meth.
Ethyl propyl benzol	100	71	99	110
Diethyl benzol	95	67	97	107
Aviation benzol	81	60	94	104
Dehydrog. Aromatics 150-175° C	80	59	93	103
Dehydrog. aromatics 175-200° C	77	55	92	101
Iso-octane	60	52	100	101
For comparison: high performance motor fuels				
O.N. 87 aviat. gasol. fr. bitum. coal + 0.09%/vol. Pb.	44	33	88	91
O.N. 100 motor fuel with 50%/vol. iso-paraffin + 0.09%/vol. Pb	56	49	101	104
Aromatization gasol. fr. bit. coal @300 atm. +0.12%/vol. Pb.	64	50	90	100
Aromatization gasol. fr. pitch @700 atm. + 0.12%/vol. Pb.	80	59	93	103
Pure iso-octane + 0.09 %/vol. Pb.	72	67	114	115

Note:
A tetraethyl lead addition of 0.12%/vol. should not be exceeded, because larger quantities may cause valve corrosion and ignition trouble due to lead deposits.

The strong dependence of aromatic fuels on the excess air coefficient λ shown in Table 3, can be considerably relieved by the operating conditions of the motor. F.A. Schmidt has shown a way to avoid a drop in overload capacity in the lean mixture range by repeated injection.

The "ring process", developed by us, offers another possibility. In this process, ignition is not effected by a spark plug, but by the injection of special substances developed in our laboratories. To our surprise, we found that the strong dependence of aromatic fuels on excess air is reduced by this process, so that in the lean mixture range a higher overload, up to 10%, can be applied than with spark plug ignition, with consequent flattening of the overload curve. In order to use this process it is merely necessary to increase the density ration to 1:8, which is already being done in practice, at least in part, to obtain a low specific consumption.

PRODUCTION OF HIGH PERFORMANCE AROMATIC MOTOR FUELS

Catalytic pressure hydrogenation in normal operation yields good auto gasolines from coal, tars and oils. Without any change in the process, but merely by adjusting to a lower gasoline end point, aviation gasoline can be produced, which has an octane number of 87 after adding the usual quantity of tetraethyl-lead. Aviation gasoline from bituminous coal is particularly high grade, though gasoline from brown coal and petroleum can also meet the requirements of 87 octane aviation gasoline.

Contrary to the processing of oil by distillation or catalytic cracking, in which only part of the oil is converted to aviation gasoline and large quantities of other products, besides gas, are produced at the same time, catalytic pressure hydrogenation is usually worked so that only aviation gasoline is produced besides gaseous hydro-carbons. This extensive utilization of the raw material is of particular importance to Germany.

A hydrogenation plant producing auto gasoline and 87 octane aviation gasoline can be converted to the production of aromatic high performance fuels by aromatization, with only slight changes in apparatus and a change in working conditions and catalysts. Besides aromatization, dehydrogenation of gasoline also yields fuels of this kind. Dehydrogenation units can be added to distillation and other oil processing plants as well as to hydrogenation plants.

However, aromatic aviation fuels have not been made to a great extent in the U.S.A and other oil-rich countries. They concentrate on making iso-octane and other iso-paraffins, particularly by polymerization and alkylation. Polymerization is based on the iso-butylene obtained in large quantities in the cracking process, which is converted to diisobutylene in the presence of a catalyst and then hydrogenated to iso-octane. Polymerization is closely related to alkylation, in which process butylene is brought to reaction with isobutane.

Because of its limited petroleum resources, Germany has no extensive cracking industry, and the isobutylene required for iso-octane production ~~must first be produced from other raw~~ materials. Of these, we might mention isobutyl-alcohol, synthetically produced from CO and H_2, and the off-gases from pressure hydrogenation and gasoline synthesis. While isobutylalcohol may easily be dehydrogenated to isobutylene, the conversion of the C_4 fractions of the off-gases mentioned to isobutylene is an expensive process, whether it be by dehydrogenation or isomerization. These off-gases consist of saturated hydrocarbons and must be completely dehydrogenated for polymerization. This very expensive process can be partly by-passed by alkylation.

Since the raw materials for iso-octane production are available in Germany only to a very limited extent, synthetic production of iso-octane from CO and H_2 has been taken up. However, in order to obtain large quantities of high performance fuels, the production of aromatic fuels by pressure hydrogenation takes first place.

Two processes are available for this end, i.e.:

Aromatization and
Dehydrogenation.

For a better understanding of the production of aromatic fuels, Fig. 2 indicates the position of the equilibrium between hydrogenated and aromatic ring systems in two examples. It shows that with cyclohexane benzol and methylcyclohexane toluol @ 50 atm. pressure and in the presence of catalysts, which adjust the equilibrium, hydrogenation predominates in the temperature range between 400 and 450° C, while at higher temperature between 460 and 560° C the equilibrium is on the side of aromatic products. It is, therefore, possible to obtain more or less hydrogenated products by regulation of the temperature. The position of the curves also indicates that dehydrogenation is easier with increasing molecular weight.

As shown in Fig. 3, a slight increase in H_2-pressure shifts the equilibrium sharply to the side of hydrogenated products. This means that under normal conditions of catalytic pressure hydrogenation and adjustment of the equilibrium at 200 atm. or more, aromatics can be obtained only in slight concentration, even if the basic character of the raw material is aromatic.

However, the formation of aromatic gasolines from H_2-poor middle oil is possible by aromatization at 200 to 700 atm. H_2-pressure and temperatures of 500° C and above with suitable catalysts, which split the middle oil with as little gas formation as possible. The partial oil vapor pressure should properly be higher than in benzination. In conformity with the above conditions of equilibrium, the middle oil is more aromatic than the gasoline. It is important to guide the reaction so that no unsaturated combinations take place, which would cause troublesome condensations on the catalyst, because the catalyst in aromatization, just as in benzination, must last about a year.

Middle oils from bituminous and brown coals, as well as H_2-poor, asphalt base or cracked petroleum middle oils can be processed by aromatization, though it is less suitable for processing H_2-rich oils. The concentration of aromatics depends upon the raw material. Bituminous coal, for example, at 300 to 600 atm. and somewhat above 500° C will yield a gasoline with 50% aromatics. It is thus possible to produce aromatic gasoline where the equilibrium is far on the side of hydrogenation products by choosing suitable catalysts.

High performance motor fuels can be produced by aromatization from suitable middle oils in apparatus almost exactly the same as used in benzination. By comparison, gasolines of any origin can be converted to fuels rich in aromatics by dehydrogenation in comparatively simple apparatus added to hydrogenation or any other method of gasoline production.

Temperatures of about 300° C at a pressure of 50 atm. or less and suitable catalysts are used for aromatization. Aromatization catalysts last a long time, while dehydrogenation catalysts must be regenerated almost every other day. Regeneration requires about one fourth of the total time.

The poorer in H_2 the gasoline to be processed is, the easier dehydrogenation takes place, i.e. the losses are smaller and the aromatic content of the DHD product is higher. It is even possible to convert the purely paraffinic Fischer synthesis gasoline to gasoline rich in aromatics by dehydrogenation, but higher temperatures must be used and greater losses by gasification must be figured on. The gas losses equal about 15% with gasoline from bituminous coal and about 20% with gasoline from brown coal, if an aromatic concentration of 50-60% is desired. The aromatics from the higher fractions are always enriched. The highest concentration, 90% and more, can be obtained by DHD of aromatization gasolines.

Examples of high grade fuels from bitum. coal middle oil are given in Table 4.

Table 4

	Benzination		Aromatization	
		Fraction 90-180° C Dehydrogenated		Fraction 120-190° C Dehydrog.
Spec. Gravity	0.730	0.794	0.803	0.830
% - 100° C	57	42	32	20
Endpoint, °C	153	182	167	186
Aromatic Content, %	7	60	52	68
Oct. No: Res. Method	75	96	89	99
Mot. "	73	83	78	86
M.M. + 0.12% Db	91	94	91	94

The first column shows a product produced by benzination from bitum. coal middle oil freed of nitrogen and sulfur pollutions by pre-treatment with a strongly hydrogenating catalyst and then processed with a strongly splitting catalyst. Commerical aviation gasoline with an octane number of 87 and an end point of about 150° C is produced this way.

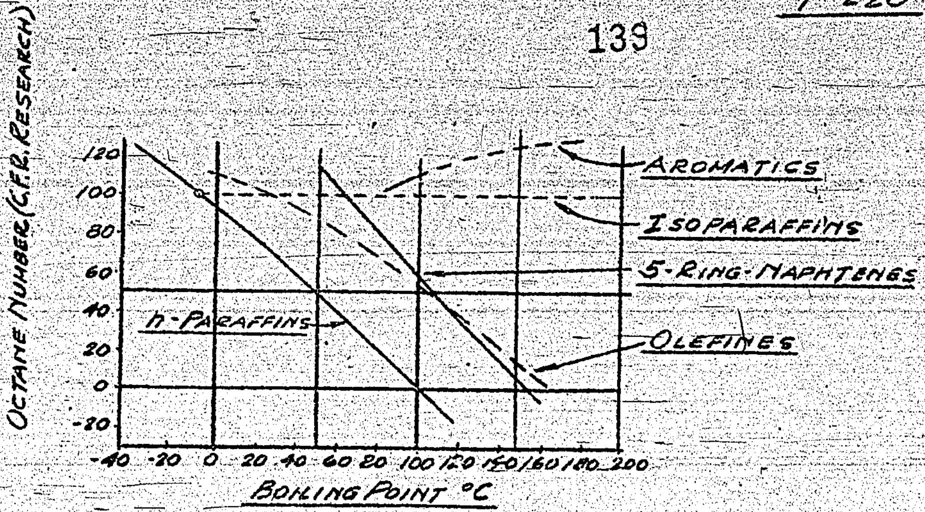
The second column shows a product processed from a gasoline with an end point of about 180° C with the same catalyst. The fraction 90-180° C, then dehydrogenated, and the constituents boiling to 90° C mixed with it. This is a distinctly high grade fuel, superior in performance to commercial iso-octane gasoline with an octane number of 100.

The third column shows a product produced by aromatization with a strongly splitting, weakly hydrogenating catalyst.

The last column shows a product produced by dehydrogenating the fraction 120-190° C of the aromatization product to about 85% aromatics and then mixing it with the previously separated light constituents.

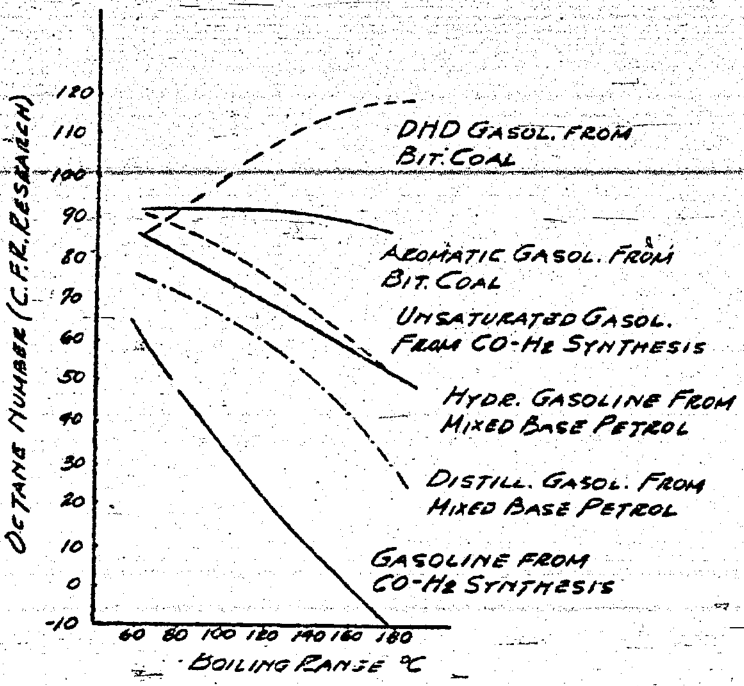
A comparison of the octane numbers of their individual fractions with those produced by other methods shows the importance of the production of motor fuels rich in aromatics, see Fig. 4. The octane numbers are lowest for paraffinic base gasoline from CO-H_2 synthesis and drop with rising boiling point. By subsequent splitting and increased concentration of unsaturated, the octane, number may be appreciably increased but even then the drop in values with rising boiling point is parallel to the original synthesis gasoline. It may be observed that aromatic gasoline from bitum. coal maintains a comparatively steady octane number with rising boiling point, contrary to the other gasolines. But the best of all is the DHD-gasoline from bitum. coal, with a high octane number not only in the low boiling range but increasing with rising boiling point.

The particular characteristics of aromatic fuels, such as high anti-knock value, good behavior in the overload motor, and high heat value per liter, justify their introduction as high performance fuels by all means at hand, since they may be produced in large quantities from German raw materials.



OCTANE NUMBER & BOILING POINTS OF VARIOUS HYDROCARBONS

FIG. 1



OCTANE NUMBERS AND BOILING CHARACTERISTICS OF GASOLINES OF VARIOUS SOURCES

FIG. 4

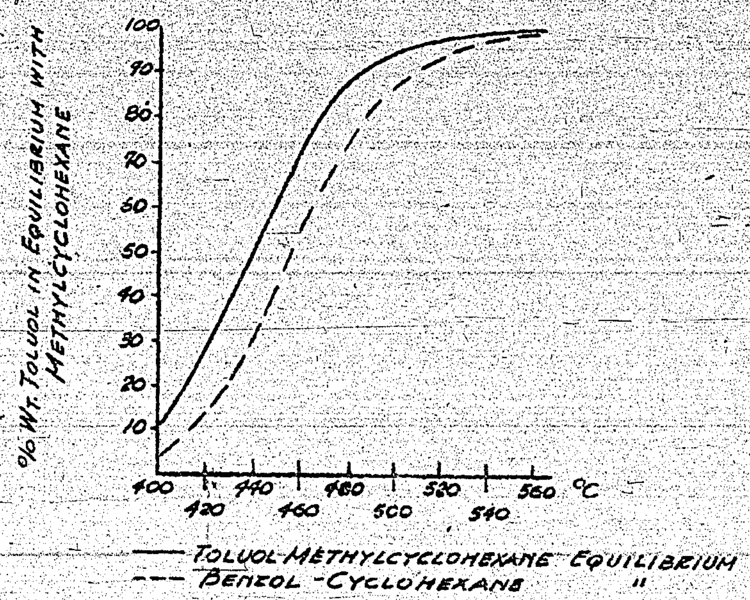
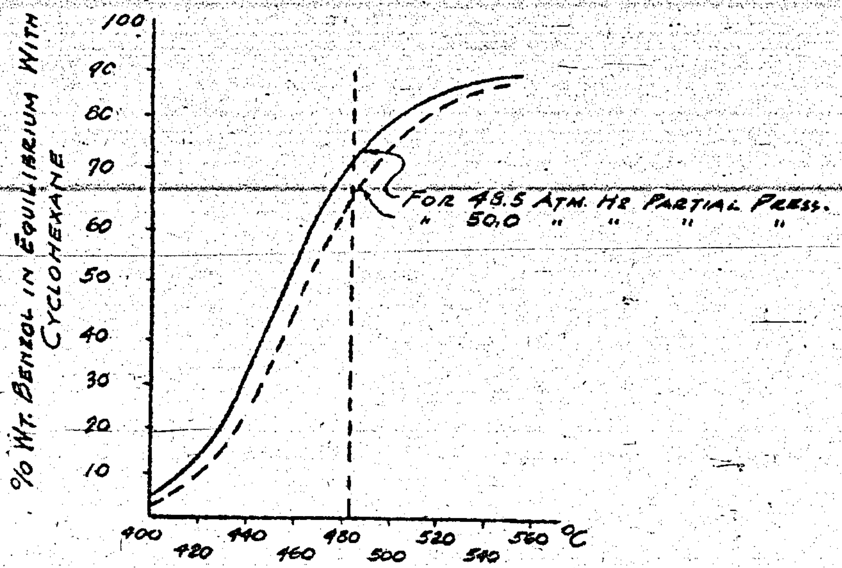


FIG. 2



Benzol Cyclohexane Equilibrium

FIG. 3

TOM Reel 168
Frames 501-522

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

T-221

ADSORPTION AND DESORPTION

A paper presented at the Meeting on the "Analytical and Preparative Separation of Hydrocarbons" on April 5, 194?.

By Kurt Peters.
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Contents:

The separation of gases and vapors by means of sorption media is a solved problem. The method of operation has, however, not found as yet as much application for the separation and preparation of pure gases as may be expected from the excellent results obtained with it.

A brief review of the practical experience and theory found in a series of experimental work on adsorption and desorption may therefore be of service as a stimulus for further research in this field.

Preparation of Pure Gases by the Desorption Method.

Adsorption and desorption deal with rather complicated processes, a recognition of which would be of material benefit in their application. This was the reason for my starting in 1928 experiments intended to clear the adsorption phenomena. The study of the laws in their simplest and clearest form, undisturbed by the complex phenomena of chemiadsorption, was done in experiments with inert gases, especially with argon, crypton and xenon. The Linde Ice Machine Company has furnished me with about 35 mls each of about 90% pure crypton and xenon. However, these gases were required in their pure form for adsorption experiments, and the concentration methods known at that time proved inadequate, especially with the small amounts of material available and the high cost of the material (1 ml of these gases at normal pressure and temperature was priced then at RM. 30.) and a loss-free separation was therefore necessary.

The assumption was made of the existence of a critical temperature range for all gases, below which the gas is so perfectly adsorbed on activated charcoal, or any other adsorbent, as to be practically non-desorbable, while the desorption was possible above that temperature; the following method of separation of the inert gases was accordingly selected 1/*:

The mixture of argon, crypton and xenon were brought in contact with a sufficient amount of activated charcoal, to have not less than 1 g. charcoal for every 10 mls of gas. (The charcoal had been previously freed from gases by heating to 400°C in vacuum). The coal was then gradually cooled to the temperature of the liquid air, and the gaseous mixture was quantitatively adsorbed. The temperature of the activated charcoal container was then gradually raised under continuous evacuation with a mercury vapor jet pump, followed by a mercury piston pump 14/, and the different fractions of the evacuated gases received separately. We have found that the three components of the gas mixture could in this way be obtained in an absolutely pure form.

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*References at the end of the article.

There were temperature ranges between the desorption temperatures of the individual gases, where no trace of any gas was desorbed from the activated charcoal. The melting points and vapor pressures of the crypton and xenon obtained in this way differed greatly from the values found in literature. The melting point of crypton was found to be -157°, against -169° given at that time, and of xenon at -112° against the older value of -140°. A few years later precision measurements made at the Physical-Technical Reichsanstalt with pure crypton and xenon confirmed the values found by us, proving that this method of separation actually did produce pure gases.

The method of separation was frequently tested in this way, and permitted us to work for two years with the small amounts of crypton and xenon available without suffering any losses.

The principle of separation of any gases by the above method of adsorption, followed by desorption, was suited to a quantitative separation. Occasionally the method must be especially adapted to specific requirements. Activated charcoal may for instance be replaced with any other adsorbent, such as silica or alumina gels, and the fractionation done by freezing or by adsorption instead of a combination of pumps as described.

In addition to the separation of the inert gases, the method was also used for the separation of gaseous hydrocarbons 7/.

Results of Measurement of Adsorption of Pure Gases.

The following results found in these adsorption measurements were worthy of notice:

1. Corresponding states of gas adsorption. The adsorption isotherms of the inert gases may be very accurately represented within a very broad temperature range above, and occasionally below, the critical temperature, at pressures up to 100 mm mercury by the Ostwald parabolic equation of the adsorption isotherm, which in the notation of Freundlich has the form of $a = \alpha \cdot p^{\frac{1}{n}}$.

This would have led us to expect, in contradiction to our above mentioned experience, that at $p = 0$, "a" would be always equal to zero, i.e., that in vacuum all the adsorbed gas will be desorbed, regardless of the temperature. We have found, that as the temperature drops, the adsorption coefficient α becomes gradually larger, and suddenly becomes very much larger in the region of the critical temperature. This is true for all inert gases, and an identical curve may be used for all inert gases to express the relationship between temperature and adsorption, when the temperature is expressed in fractions of the critical temperature 12/. A remarkable drop in the rate of desorption, or an increased permanency of adsorption near the critical temperature goes parallel to the enormous increase in the amounts of adsorbed gas. Below a certain temperature in the neighborhood of the critical temperature, and which may be called the critical sorption temperature, it becomes impossible to extract measurable quantities of gas even when pumping for days to the highest vacuum which can be produced.

We may deal here with a change from the surface adsorption to a capillary condensation.

We may approximately predict the most favorable temperature for the sharp separation of any gases on the strength of this observation. It must be noted, however, that this critical sorption temperature may differ considerably from the critical temperature of a particular gas. It depends on a number of different factors, in particular on the kind of adsorbent, and on the number and kind of simultaneously adsorbed other gases. We may cite here by way of example, that propane is completely desorbed from activated carbon only at temperatures of 0° C, when adsorbed alone, but that desorption already proceeds at -10 or -20° when different amounts of butane were absorbed simultaneously.

It has been found with the chemically completely inert gases, that when the adsorption laws are considered under proper corresponding conditions, they can be expressed by very simple formulas for all the members of the series, at low pressures and for very wide temperature ranges. For chemically reactive gases the adsorption laws are considerably more complicated.

2. The effect of molecular structure on gas adsorption. The molecular structure, rather than the molecular weight, affect adsorption. Methane and crypton show qualitatively as well as quantitatively a remarkably similar adsorption behavior, although the molecule of methane is some five times lighter, than crypton. In the adsorption of this simplest hydrocarbon molecule there are forces transitional to chemosorption in addition to the purely mechanical forces of adsorption of the inert gases. The adsorption of methane is never-the-less similar to that of the inert gases, just as the molecule of methane is structurally similar to that of the inert gases.

Conditions in hydrocarbons with two or more carbon atoms are still more complicated. In addition to the fact that the adsorption isotherms of these gases can no longer be represented by a simple parabolic equation, like the adsorption isotherms of the inert gases and methane, one may also observe remarkable differences between the individual adsorption and desorption isotherms. The adsorption equilibrium of the higher hydrocarbons is not strictly reversible as is the case with inert gases, and gases having the structure of inert gases. These phenomena may be explained by the assumption that complicated molecules are adsorbed in different manner by the same adsorption medium 11/.

There is, in addition to the mechanical forces responsible for the adsorption of inert gases, also an active interchange between the chemical forces of the gas molecules and the adsorptive surface forces. In the already adsorbed state, the chemical forces of these substances still remain active to some extent, and will not merely reduce the adsorbing power of the medium, but also change with respect, e.g., to its selectivity.

These phenomena do not affect the fundamental property of separation of gases by adsorption, followed by desorption. We may, however, treat the adsorption medium, before using it for a definite separation, with other reactive substances, e.g. with halogen compounds, oxygen or nitrogen-containing or unsaturated compounds, sulfur dioxide, etc., or use such substances to displace the adsorbed substances. There exists finally the possibility to affect the vapor pressure of any adsorbed substance and produce a shifting of its desorption temperature.

Advice for Practical Separation of Gases.

1. Density of Charge. As a result of the continuous change in the adsorptive power of a medium with an increasing load, the separation is the sharper, the larger the amount of the adsorbent used. We may use as a general directive the statement, that with a less than complete formation of a monomolecular cover layer by the higher boiling components the separation as a rule is excellent if good separations can still be obtained with still higher concentrations.

The smaller the amount of adsorbent used for adsorption, the smaller is also the gap in the temperature scale where no gas is desorbed, before the gap disappears entirely. We get only a more or less strong enrichment in the fractions, instead of any sharp separation.

To separate a large amount of a more volatile gas from a smaller amount of a less volatile one requires much less of an adsorbent than is required for the separation of smaller amounts of more volatile from larger amounts of less volatile substances. A pre-fractionating may be advisable in such a case. The sharpness of separation of two consecutive members of a homologous series, e.g. of paraffin hydrocarbons, becomes smaller with increasing molecular weight of the substances, and becomes still less in case of a mixture of different isomers. But even in difficult cases, say in the separation of isotopes, 10/, a good separation can be obtained, when in addition to the directions already given, the following are intelligently applied:

2. Uniformity of Load. A uniform coating of the active surface of the adsorbent and a good temperature distribution inside the adsorbent are especially important during desorption. If adsorption is made by cooling the adsorbent to low temperature before bringing it in contact with the gaseous mixture, a nonuniform load is readily produced, which will result in a failure in the subsequently attempted separation. Certain layers of the adsorbent will be heavily loaded, while distant ones will carry but a light load. During desorption only a fraction of the adsorbent will be used, and a large amount of it will behave during the desorption like a small amount carrying a large load. When the adsorption vessel is very strongly cooled before the adsorption, the additional danger will be present of rapid condensation of the condensible constituents of the mixture upon the walls of the vessel, without ever reaching the adsorbent. During the subsequent slow warming, these non adsorbed little-volatile constituents thaw out first, evaporate and will be present in the first fractions distilled, before desorption will have begun. On the other hand, were one to operate in the manner described above, and bring the gaseous mixture in contact with the adsorbent at relatively high temperatures, and only then gradually cool the whole vessel, all the active surface becomes uniformly charged, and the constituents will be set free uniformly and in proper sequence during the desorption which will follow.

3. Rate of Desorption. As already mentioned, the rates of adsorption and desorption become lower at lower temperatures, and below the critical sorption temperature equilibrium becomes as a rule very slowly established. At a given temperature, the higher boiling constituents of a mixture are occasionally adsorbed more slowly, than the lower boiling. This may lead to errors when desorption is begun without giving sufficient time for adsorption. Should one wish to separate higher boiling gases present in low concentration from lower boiling gases, by passing a stream of gas over the adsorbent, care must be taken about selecting a sufficiently long time of contact.

(One page of the original missing in the microfilm.)

5. The Gas Flushing Method. One may also obtain a good heat transfer by working instead of high vacuum in a stream of gas either not adsorbed, or but little adsorbed under the conditions used at atmospheric pressure, e.g. hydrogen, nitrogen, neon or helium. This method of operation offers the advantage of permitting to do without high vacuum equipment, the use of which is frequently disliked in industrial laboratories. A stream of an auxiliary gas permits to carry out the desorption at very low

partial pressures of the constituent to be separated, as is the case in the vacuum desorption. The sharpness of the separation is hardly at all affected by the adsorption of the auxiliary gas, as in the displacement methods, where steam or carbon dioxide are used as the auxiliary gases. Excessively large volumes of gas are avoided by circulating a moderate amount of the auxiliary gas through the adsorption vessel and then through a replaceable low temperature trap for the adsorption of the different desorption fractions, and gradually increasing the temperature of the adsorption vessel until the desorption is finished.

6. Practical Temperatures. The most convenient temperatures are found by gradually increasing the adsorption vessel temperature. As a general rule , the known critical temperatures of the gases offer a convenient starting points. The separation of neon and helium, 9/ or of the isotopes of hydrogen 10/ is done at temperatures below -220°C. On the other hand, a quantitative separation of the gaseous hydrocarbons is produced in the very convenient temperature range of -80° to + 100°.

A simplification of the process of separation of mixtures of hydrocarbons is possible, when no quantitative separation of every component of the mixture is required. It is sufficient then to break up the mixture into fractions, each of which contains not over two saturated and two unsaturated hydrocarbons, because such mixtures can be readily analyzed by other methods. Working in this manner, special thermostats can be dispensed with, and the process arranged by using only such constant temperature baths, which can be found in any laboratory, such as carbon dioxide, ice-salt mixture, ice, and water baths at different temperatures. The possibility of extraordinarily accurate analysis of complicated mixtures of hydrocarbons using this method is proven by numerous experimental runs (5/ to 8/.) They show also that the desorption method is particularly suitable as a micro method.

The analysis of a bituminous coal of the Minden colliery for the higher gaseous hydrocarbons and the little gasoline present in the coal has already been very accurately done by the desorption method in 1932, when the experience was as yet very limited, although in the small gas samples obtained by grinding in vacuum only 1.8% by volume of pentane and 1.4% hexane were found.

The size of the gas samples needed for analysis will depend primarily on the auxiliary physical and chemical methods necessary for the control of the desorption method and for the preparation and identification of the desorption fractions produced.

7. Auxiliary Methods. In the absence of auxiliary gases, desorption is made into the highest vacuum producible. When the size of the gas sample is sufficiently small, or the evacuated space sufficiently large, the progress of desorption and the volume are judged by following changes in pressure. 13/. Every fraction produced can next be collected from the evacuated space by evacuation or freezing. When evacuating with a vacuum pump, the fractions can be measured volumetrically.

The identification or analysis of the individual fractions may be made by any method used in gas analysis, such as the determination of molecular weight, density with the gas suspension balance, (1/, 7/), spectrum analysis 13/, absorption and combustion analysis, 7/, 8/, vapor pressure measurements 7/, also by measurements of heat conductivity, melting point determinations, refractive index, etc.

In the preparation of pure gases the problem of obtaining a 100% yield may be of secondary importance. The object in such cases is quickly reached, when a gas, crudely refined by chemical means or by distillation, is broken down into three fractions by desorption, discarding the small first and last fractions, which contained all of the impurities. If a single desorption produced a middle fraction not yet sufficiently pure, a repetition of the process is certain to bring about the desired results. The desorption method has also proven very valuable for the removal of the last traces of impurities in gases obtained by other methods.

8. Analysis for Traces. Adsorption and desorption method is particularly well adapted for the detection of traces of contaminants. Should the intention be to determine quantitatively very small amounts of some high boiling constituent, a very small amount of the absorbent is sufficient for a quantitative separation by adsorption. The correct choice of the adsorption temperature is a prerequisite for the success of such an analysis, as well as a sufficiently long time of contact with the adsorbent. Should the amounts of contaminants be very small, when dealing, e.g. with traces of hydrogen sulfide, carbon bisulfide, acetylene or higher hydrocarbons, organic vapors, etc., in air or industrial gases, work is done at atmospheric pressure with a relatively low rate of flow. Results are obtained more quickly, if adsorption can be carried out at increased pressure, or when it is possible to partially liquefy the gases. The adsorption of the higher boiling constituents proceeds quantitatively from liquefied gases as well. The following experiment with radium emanation shows how small the amounts may be. The amount of the unabsorbed emanation was very accurately followed up by electroscopic

measurements. A small amount of radium emanation was dissolved in 2 liters of liquid air, and a small wire gauze basket with a few grams silica gel was immersed in it. The radium emanation was quantitatively absorbed from the liquid air in the course of a few hours. In this case the proportion of concentration of the emanation to air amounted to $1 : 10^{14}$. Considerable amounts of crypton and xenon were in the same way obtained in the course of time from liquid air, by suspending a small basket of silica gel in the liquid air container before using it as a refrigerant in the laboratory.

9. <u>Continuous Method of Separation</u>. When a definite amount of a gaseous mixture is made to pass a vessel filled with an absorbent, the different layers of the absorbent from gas inlet to gas outlet will be successively enriched in the direction of the flow first with the higher boiling constituents, then with the lighter components, similar to the rings formed in chromatographic analysis which permit the identification of the different components of the mixture. Should the adsorption space be suitably subdivided into several containers connected successively, it becomes readily possible to concentrate in each compartment one component of the mixture. In accordance with the principle of displacement, when the mixture is kept passing through the adsorbent, the zones will keep moving towards the outlet, until finally even the heaviest components will break through at the end.

A continuous separation of all the constituents of a mixture in a relatively high concentration can be worked out using this principle and working with a movable adsorbent. A sluicing arrangement is used, similar to that used industrially for grainy material, which keeps changing during the course of a chemical operation. Should this principle be used for the separation of gases by adsorption, a number of such sluices is connected serially, and the gaseous mixture is made to pass through it. Each such vessel is independently supplied at the end with fresh adsorbent, while at the other end a similar sluicing arrangement withdraws the adsorbent of any one component of the gaseous mixture and introduces it into a desorbent for this component. This arrangement permits keeping each individual container for adsorbents at the optimum temperature for the adsorption of the component, and regulate the amount of adsorbent in such a way, that the individual gas constituents are at all times found near the end of that adsorber. Should a single operation immediately produce very pure adsorbed materials, intermediate adsorbers can be introduced into which the break-through zones are shifted. Different, perhaps selectively working adsorbents may be used in the different adsorbers.

Conclusion.

The problem of separation of gases by absorption and desorption may be considered solved in principle; however, experimental results shown here and their discussion indicate, that many questions still remain to be answered, and that the practical application of gas adsorption to the fine separation of hydrocarbons still remains in the beginner stage. Were we to name just a few of the unanswered question, we would mention the application of the method for the separation of the higher hydrocarbons, e.g. in the boiling range of gasoline, in particular the separation of the paraffin isomers, except the separation of normal and iso pentanes. An exhaustive study of the effects of the molecular structure of the adsorbed substances and the structure of the adsorbent upon adsorption, also the study of adsorption of mixtures, promises results having not merely a theoretical interest but practical applications as well, especially in finding selectively acting adsorbents.

W. M. Sternberg

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BUREAU OF MINES
TORRANCE, CALIFORNIA

THE SIGNIFICANCE OF "HOT CIRCUIT" OF THE HOLD FOR THE LIQUID PHASE STALL.

A communication by Dr. Frese. (For limited circulation)

The purpose of the "Hot Circuit" of the liquid phase stall is to return the HOLD rich in solids to the fresh feed of the circuit, avoiding larger heat losses and without the expenditure of much power. It can be advantageously added to the feed in front of the second pass of the preheater. It is particularly suited to feeds, such as tar, which contain no or very little solids, and where accordingly large proportion of the HOLD need not be sent to the recovery of the residue. This feed requires chiefly that catalyst be introduced into the circuit, and as a result a high concentration of the catalyst is produced immediately in the first converter.

There is, however, no such advantage with feed with high content of solids and ash right at the start, as, e.g., brown or bituminous coal. With bituminous coal containing 5% ash and 3 - 4% coal particles not utilized in the hydrogenation process, as well as two percent catalyst, it became necessary, that with a 25% solids content of the HOLD at least 4 x $\frac{11}{2}$= 22% of the injected paste (50% coal - 50% oil) be sent to the recovery of the residue.

In such case the hot circuit assumes the task of producing a greater security of the process. This is the result of better mastery of the "swelling zone" by mixing in the critical zone of the preheater the 50% coal paste with 25% of HOLD. The more sluggishly reacting HOLD oil moderates the hydrogenation reaction in the converter proper, reducing the undesirable "passing through" the converter. This greater safety brought about by the return of a certain proportion of the HOLD results also in a smaller throughput through the stall, as found in my tests in 1937 in Leuna, because the rate of passage through the stall is increased and the paste remains the shorter time inside the converter.

The disadvantage of the "hot circuit" consists in its relatively high cost of the complicated equipment, with the hot-oil-operated valve assemblies, pumps, many valves, in part water cooled, a complicated metering installation and also all the troubles connected with such equipment. Should there be trouble, with the "hot circuit" suddenly getting out of use, the whole stall operation is disrupted. This is just the place where the danger of "passing through" and of coke formation inside the converter is the greatest because the preheater is set for an amount of gas necessary for larger flow, which is suddenly greatly reduced. As a result, the converter intake temperature will suddenly rise very high, and the heavy oil of the circuit will not be present to moderate it. For this reason, wherever the "hot circuit" was used, there was provided a 100% reserve of spare valve assemblies and pumps.

As far as is known to me, Leuna has discontinued within the last years the use of the "hot circuit" in its brown coal stall, while it was retained in the two bituminous coal plants at Scholven and Gelsenberg. However, Leuna as well as Scholven and Gelsenberg added some uncompressed HOLD to the fresh paste, using up additional amounts of energy, but preferring this safer way.

Arrangements for pumping over for the "hot circuit" at the small demonstration plant in Louisiana are relatively expensive with the above mentioned safety installation consisting of a 100% reserve of pumps and valves. Stopping sudden disturbances is very difficult without the reserves, regardless of whether a resumption of the "hot circuit" operations is possible after long repairs (depositions in the pipe lines). While as a general rule, a sudden shut-down of the "hot circuit" is rare, because a slowing down in use is caused by valve troubles, it must never the less be taken into consideration. The shutting down of the "hot circuit" is the most inconvenient, when the stall temperature had for certain reasons increased. In this case the circulating feed will be unavailable just when most needed.

As a general rule, a "hot circuit" with the required reserve installations offers certain advantages in power consumption of large plants, as well in introducing a certain safety factor, but it also carries with it certain dangers, which must not be overlooked.

The installation costs will be reduced and a safer way will in my opinion be chosen, if in this small installation the intended HOLD addition to the coal paste after complete pressure release, be increased, expending for that purpose power on pumps, but entirely omitting the pumps necessary in the "hot circuit". It becomes then possible to run tests on the most favorable amounts of HOLD to add to the paste. It may happen, that a very small amount will be found sufficient, and possibly even none at all. As a general rule, a higher coal concentration requires a greater HOLD addition to the circuit, i.e. a high coal concentration is thinned out before introduction into the converter. Were one to select a lower coal concentration, the addition of HOLD may be reduced. There is no doubt about a higher yield from a paste with no HOLD addition because of the longer stay in the converter. The best way, with the greatest safety for stall operations, will have to be found. A paste with 40 - 42% coal, and containing a considerable proportion of heavy oil from the centrifuge oil should be used, in my opinion, either without any addition of HOLD, or only with a small addition. Such a paste will offer the advantage of permitting using it with a heat exchanger. To clarify all these questions for a subsequent large installation, it would be advisable to select not too small a preheater in the demonstration plant, to permit it to heat up additional amounts of HOLD (up to 30 - 35% HOLD to the total coal paste).

There is an additional reason for omitting the "hot circuit" in Louisiana. A continuous flow of flushing oil is required in four places of the "hot circuit" (in the by-pass line and in the flow meter). According to my recollections, this amount will be at least 400 - 500 li/hr. The total recirculation of the "hot circuit" will only amount to 1000 li/hr, and the flushing oil alone will amount to about 50% of it, changing thereby the whole picture.

DIRECTIONS FOR SERVICING THE "HOT CIRCUIT" (v. sketch)

Starting.

1). After repairs on the pumps or valve assemblies, the pipe lines LL and LR and the valves 16 are to be flushed with nitrogen through the valves 17 -> 6 and 5 -> 7, the same for the valve assembly through the valves 16 -> 6 -> 5 -> 7. The equipment is then ready for operation.

2). The pipe lines LL and LR are next filled with flushing oil from the surge tank to stall pressure. Attention must be paid to have all nitrogen removed from the pipe line through the valve 9 placed at the highest point. No gas bubbles should be permitted to remain in the pipe line.

3). The pumps are started with the by-pass open (valve 18). the pressure release valve 19 is opened for a short time. The pump is to be set for small delivery.

4). The valve assembly is connected with the stall as soon as the level is reached in the hot catchpot after starting the stall or after repairs. For this purpose, the two suction valves 1 and 2, and the pressure valves 3 and 4 are opened. The pump by-pass 18 is closed.

5). The pressure release valve 19 must be opened and the two shut-off slides inserted into the by-pass pipe line. A small amount of flushing oil is continuously passing through the balancing pipe line (Pendelleitung). The output of the pump is to be gradually increased to the required amount.

6). The amount of the "hot circuit" is regulated by the flow meter on the pressure side (flushing oil to be continuously passed through valves 14 and 15.)

Shutting Down.

The shutting-down may be required by:

a) normal cold operation of the stall;

b) trouble with pump or valve assembly. The trouble will be indicated by reduction in the flow meter readings, or by the drop in temperature in the hot circuit.

In case of b), the two valve assemblies and the reserve pump are immediately put in operation as described above, and the amount of hot circuit slowly increased to the prescribed level.
After this has been accomplished, the pump formerly in use is shut down as follows:

1) The pump shut down and the flushing oil turned off (valve 10)

2) The valves 1 and 2 in the suction side of the circuit are turned off.

3) The valves 3 and 4 in the pressure side of the circuit are turned off.

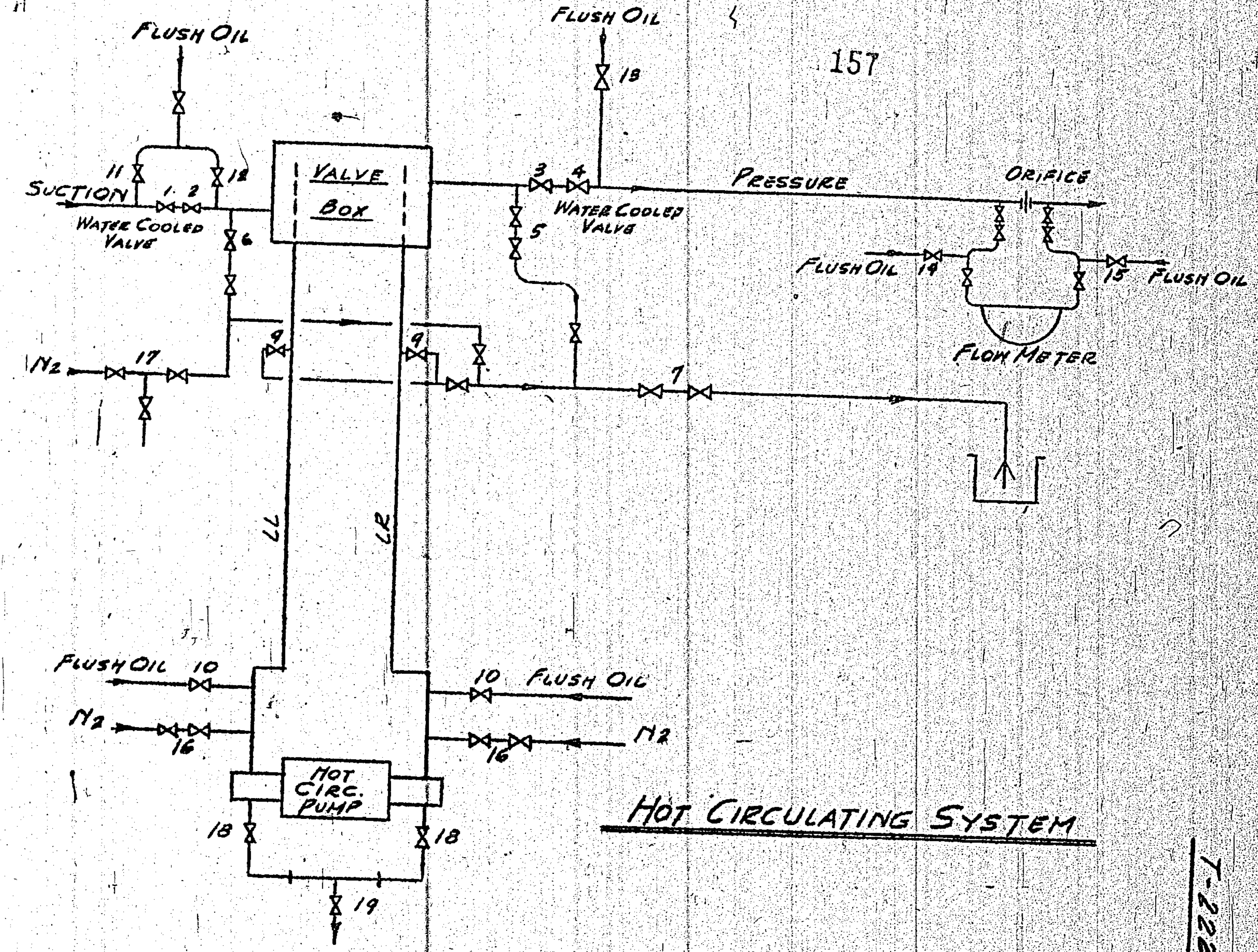
4) The valve assembly is flushed with flushing oil through the valves.12 -> 5 -> 7, and then with nitrogen through 16 -> 5 -> 7.

5) Emptying the pipe lines LL and LR through the valve 19 after inserting the blind gaskets in the pump by pass lines. Flushing with nitrogen through 16 -> 5 -> 7 of 16 -> 19.

6) Before the pumps or valves are sent away for repairs, blind gaskets are inserted in the two suction lines LL and LR or

between the valve 2 and the valve assembly or the valve 3 and the valve assembly. Should there be no reserve valve assembly or pump, the valves 1, 2, 3 and 4 are closed to maintain the suction and the pressure sides of the hot circuit under a continuous flow of a small amount of flushing oil through the valves 11 and 13.

W. M. Sternberg.



HOT CIRCULATING SYSTEM

T-222

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

T-223
KCBraun
1-31-47

PROCESS FOR CLEANING AND UTILIZATION OF WATERY FLUIDS, PARTICULARLY OF WASTE WATERS

German Patent 534204

Class 85c, Group 1,

10 Feb. 1928

Issued to

Carbo-Norit-Union Verwaltungs G.m.b.H.

Frankfurt a.M.

By

Dr. Anton Mackert, Frankfurt a.M.

The invention described herein concerns the cleaning of watery fluids, particularly of industrial waste waters, and the recovery of their constituents by the use of adsorption media, such as active carbon, with simultaneous regeneration of the exhausted adsorption media.

A process is already known, according to which the waste waters containing phenols of coke plants is brought into contact with active carbon and recovering the adsorbed constituents by removing them from the carbon with steam, particularly superheated steam.

The disadvantages of this process are the following: The constituents recovered in this manner, when not soluble in water, such as phenol, are obtained in a watery solution, largely in such a diluted condition that their removal or further processing is very costly. This disadvantage can only partly be avoided by higher steaming temperatures, because the coal absorbs considerable quantities of water, besides the constituents to be removed, which must first be removed by superheated steam with a great expenditure of heat energy, before the desired higher temperatures can be obtained, at which the adsorbed constituents are driven off so fast that it may be recovered in suitably concentrated form.

A further disadvantage of this process is that the adsorbing power of the coal declines very rapidly, because not all constituents present can be driven off by steaming and secondary decompositions of the adsorbed constituents take place at the high temperatures, so that the adsorption media are often completely spoiled after only a few operating periods.

By using granular active coal, for example, a rapid mechanical disintegration of the coal also takes place at such high temperatures.

It has already been suggested to remove substances from adsorption media used to adsorb them from gases by treatment with solvents for these substances and then remove the residual solvents from the adsorption media by steaming. According to the process of this invention the disadvantages of the process for the treatment of watery fluids first mentioned herein are effectively avoided by the combination of the characteristic of adsorption in a watery medium with the characteristic of extraction mentioned in the second process of removing the substances from adsorption media used to adsorb them from gases by means of solvents and the further characteristic of the subsequent removal of the residual solvents from the adsorption media.

According to this invention, therefore, waste waters containing phenols, e.g. are first treated with adsorption media, such as active carbon, and the charged adsorption media then treated, preferably in a still completely soaked condition, with solvents not dissolvable or difficult to dissolve in water, which are capable of dissolving the adsorbed substances in the adsorption media, and finally the residual solvents in the adsorption media are removed from them by a simple treatment, e.g. with steam.

The process is based on the observation that the adsorption equilibrium between the adsorption media and watery solutions is entirely different from the equilibrium between the adsorption media and non-watery solutions, particularly where solutions of organic substances are concerned.

Certain active carbons, for example, in contact with a watery 0.5% phenol solution can adsorb about 25 to 30% of their weight of phenol, while in contact with a solution of phenol in benzol the same degree of adsorption is obtained only with a content of 12% phenol.

Of particular advantage in the removal of the adsorbed substances has been found to be the use of solvents which can not be dissolved or are difficult to dissolve in water, or of solvent mixtures in which one or more components possess this quality. Such solvents are benzol and carbon-disulfide, or a mixture of benzol and alcohol, benzol and acetone, etc.

It has been found that the charged adsorption media, such as active carbon, can be readily freed of the adsorbed substances by means of such solvents, even in a completely soaked condition, and that the extraction capacity of these solvents is hardly affected by the simultaneous presence of water. On the other hand, these solvents can again be removed from the adsorption media in the simplest manner, as by steaming or treating with boiling water.

The operation is preferably performed in such a manner that the waste waters to be cleaned are conducted thru the adsorbing medium from the bottom towards the top, while the treatment with the solvents and the subsequent removal of the solvent takes place in the opposite direction, from top to bottom. Several adsorption media containers may be arranged in series, if need be or desired. In this counterflow operation a high average charge of the adsorption media is obtained and a highly concentrated solution of the substances to be removed from the solvents in extraction. After separating the dissolved substances from the solvents, as by distillation, the solvents can again be used.

The main advantages of the new process are:

The water absorbed by the adsorption media in the charging does not disturb the reaction in any way, no additional energy is required to remove this water. Regeneration of the adsorption media is effected at a comparatively low temperature. Decomposition of the adsorbed substances at high temperatures and consequent fouling of or other damage to the adsorption media are entirely avoided. The adsorption media are not exposed to a too rapid or severe change in temperature and thus are amply protected. By using solvents, which cannot be dissolved or are difficult to dissolve in water, the adsorbed substances are almost completely carried off by the solvent and can be recovered from them immediately in a condition free of water.

The process at hand is generally suitable for the cleaning and utilization of watery fluids or the substances contained therein, as e.g. waste waters from coke or cellulose plants, etc. The cleaning operation may be so conducted that the cleaned waters can again be used for industrial purposes.

Active carbon can be used as adsorption medium in most cases, whereby one or another kind of active carbon may be preferred, depending upon the fluid to be treated. For example, in the treatment of waste waters containing phenol, gas or steam activated carbon has proved to be best. Otherwise the kind of adsorption medium to be used is naturally dependent upon the kind of fluid to be treated. The kind of solvent or mixture of solvents to be used for extraction is dependent upon the kind of substance to be adsorbed and removed.

The adsorption media may be used in pieces or in pulverized form. When working with granular, particularly coarse granular, adsorption media, the use of beds over 1 meter deep, or the arrangement in series of several containers, has proved to be advantageous. When using pulverized adsorption media it is likewise proper to arrange several filter elements in series.

Example:

Coke plant waste water, whose principal constituent was about 0.5% phenol, was conducted thru a layer of granular active carbon 1.5 meters deep in a direction from bottom to top, after first removing the suspended matter contained in the water. The coal adsorbed about 25% of its weight of phenol. The moist coal was then sprayed from the top with hot benzol. The content of phenol in the benzol flowing off at the bottom was about 11%. The benzol was continuously distilled in a rectification column and re-used for extraction. After the content of phenol in the benzol flowing off at the bottom had dropped to about 3%, steam @ 100° C was introduced at the top, thus driving off the benzol absorbed by the coal. In this operation, the benzol trickling through the coal bed washed out further quantities of phenol still present in the bottom of the bed. The upper portion of the coal was practically free of phenol after driving off the benzol, while the lowest portion contained only 3% phenol.

Patent Claims.

1. Process for cleaning and utilisation of watery fluids, particularly of waste waters, characterized by treating the fluids with solid adsorption media, advantageously after pre-cleaning, e.g. after removing the suspended matter contained in them, then removing the adsorbed substances from the adsorption media by treating them with solvents or mixtures of solvents, possibly at increased temperatures, and finally driving off the residual solvents remaining on the adsorption media in a suitable manner, as by rinsing with steam.

2. Process according to Claim 1, characterized by using solvents, which cannot be dissolved or are difficult to dissolve in water, or mixtures of such solvents.

3. Process according to Claims 1 and 2, characterized by charging the adsorption media from bottom to top and regenerating them from top to bottom.

4. Process according to Claims 1 to 3, characterized by deep beds of adsorption media, 1 meter or more, or possibly in several containers arranged in series.

T-224

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

KCBraun
1-31-47

PROCESS FOR THE PRESSURE HYDROGENATION OF COAL-OIL MIXTURES

German Patent 707851

Class 12o, Group 1o5

18 Jan. 1938

Issued to

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

By

Dr. Mathias Pier, Heidelberg,
Dr. Walter Krönig, Ludwigshafen/Rh.
Dipl. Ing. Hans Schappert, Ludwigshafen/Rh.

It is known that in the pressure hydrogenation of coals, tars, mineral oils, or their distillation or extraction products, the greater part of the feed materials can be preheated by heat exchange with the products of reaction and the remaining smaller portion conveyed to the reaction space without preheating or preheating with heat from an outside source.

It has now been found that in the processing of coal-oil mixtures, particularly when using bituminous coal, swellings occur from a given temperature on, particularly above about 250° C, and the mixtures become more viscous from this temperature on. This condition is directly proportional to the amount of coal in the mixture. Generally speaking, swellings appear markedly when the proportion of coal is more than 50%. However, this also depends to a great extent on the kind and character, e.g. the fineness, of the coal and oil. This property causes particular difficulties in preheating. These difficulties, for example, are such that the coal-oil mixture, particularly with a high coal content, can no longer be conveyed without danger thru heat exchangers with parallel tubes, because of a tendency to clogging. Excessive wear in the bends of the preheater tubes also appears in connection with the increased viscosity of the mixture.

These difficulties may be avoided by keeping the proportion of coal in the mixture below a certain point, which, however, should not drop below a certain limit for economic reasons, or by not grinding the coal too fine. Wear-resistant return bends have also been built for the preheater tubes. However it is impossible to preheat the coal-oil mixture by heat exchange in parallel tubes, for the reasons given above, unless the proportion of coal is held below the minimum economic limit. On the other hand if the heat exchanger cannot be used, a large amount of outside heat will be continuously required, which must be supplied by an expensive preheater. The cooling surface for the products of reaction are also relatively costly and a large amount of cooling water is required.

It has now been found that these disadvantages can be avoided, if, in using the operating method first mentioned herein, care is taken that the greater portion of the feed stock is preheated by heat exchangers and that it contains a lower proportion of coal than the other portion, which is not preheated or only slightly so.

The process is properly worked so that the portion of the coal-oil mixture with the lower coal content is brought to, or nearly to, the reaction temperature by means of heat exchangers and is then mixed with the other portion of the coal-oil mixture having the higher coal content but lower temperature, to a mixture temperature of above 350° C. The mixture is then brought to the reaction temperature in an additional preheater. Since the controlling factor for the partial stream with the higher coal content is its ability to be pumped, a high coal concentration may be chosen and the coal thruput necessary to the economy of the process can easily be obtained. The common preheater, which supplies the final, peak heat, is no longer in danger because of the reduced coal content of the mixture and because swellings are not likely to occur at such high temperatures. An additional advantage of this process is that the heat transmission is very high in case a coal-oil mixture of low coal content is used, so that the portion to be heated by heat exchange can very easily and rapidly be brought to a high temperature.

The coal content of the larger partial stream may properly equal 45-42%, while that of the smaller partial stream may advantageously equal 50-65%.

The coal-oil mixture with the high coal content can also be used entirely or partly as a cooling medium for the reaction itself and conveyed directly to the reaction space for this purpose either cold or only slightly heated. In case this mixture is to be slightly heated, this can be done in a special part of the preheater, or, if need be, in a heat exchanger, to a temperature at which no swelling occurs, say 250° C or less. The temperature range, within which swelling would occur, is quickly bridged over by mixing it with the other portion of the coal-oil mixture heated to, say, 420° C, giving a mixture temperature of about 370° C. The actual coal content in the mixture is less than that figured by the mixture rule, because a part of the coal is already liquified in preheating.

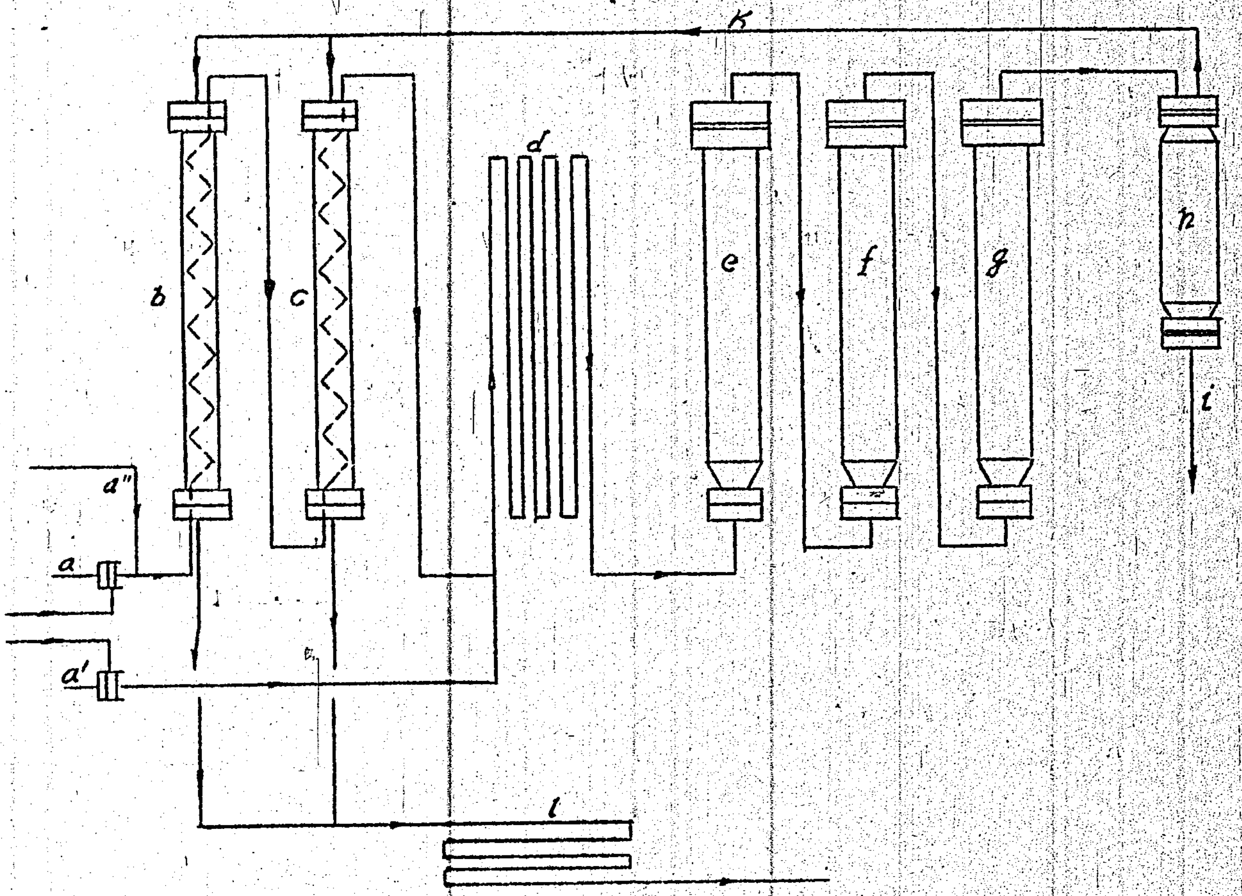
The process is further described on the attached drawing. By means of pump (a) 16 t/h of a coal-oil mixture containing 43% bituminous coal and 57% heavy oil are injected. The bituminous coal was mixed with 0.5% tin-oxalate before the paste was mixed. Thru line (a") 30000 m^3/h of H_2 is injected into the coal-oil mixture. The coal-oil mixture containing H_2 is heated to about 420° C in the heat exchangers (b) and (c). Thru pump (a') 8 t/h of a coal-oil mixture containing 55% bituminous coal and 45% heavy oil is injected. In this case the coal was also mixed with 0.5% tin-oxalate before pasting. This mixture is heated to about 120° C before injection, in order to decrease its viscosity. The two coal-oil mixtures meet before the preheater (d), which latter they enter at a mixture temperature of 360° C. The mixture is heated in the preheater to the reaction temperature, about 420° C, at which temperature it enters the reaction converter (e). After running thru the converters (e), (f) and (g), the products of reaction enter the catchpot (h), from which the liquid and solid products are drawn off at (i). The gases and vapors flow thru line (k) to the heat exchangers (b) and (c) and are eventually cooled in cooler (l), where the liquefiable products of reaction are separated. The H_2 is used again after cleaning.

Although it is known that in the pressure hydrogenation of unstable hydrocarbon oils these may be added cold or slightly preheated to highly heated stable oils before or in the reaction space, in order to avoid separations, this invention has nothing to do with that method. This invention is concerned with the pressure hydrogenation of coal, wherein two differently constituted coal-oil mixtures are used, which are brought together after heating up and which can then be further heated together from a certain temperature on without causing troublesome swellings.

Patent Claims:

1. Process for the pressure hydrogenation of coal-oil mixtures, wherein the greater portion of the mixture to be processed is heated by heat exchange with the products of reaction, while the smaller portion of the mixture is not or only slightly heated, and wherein the mixture, after combining both portions, is further heated to the reaction temperature, characterized by the greater portion of the coal-oil mixture heated by heat exchange having a lower coal content than the other portion.

2. Process according to Claim 1, characterized by heating the portion with the higher coal content to temperatures of 250° C or less.



T-224

T-225

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

KCBraun
2-3-47

PROCESS FOR PRODUCING LIQUID HYDROCARBONS FROM COAL

German Patent 715111,

Class 12o, Group 1o5.

30 Sept. 1933.

Issued to

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

By

Dr. Mathias Pier, Heidelberg,
Dr. Paul Jacob, Gelsenkirchen, and
Dr. Walter Krönig, Ludwigshafen, Rh.

It is already known that solid crushed carbonaceous substances, like coal, peat or wood, may be soaked in a catalyst solution and then subjected to pressure hydrogenation. It has, however, been found that various kinds of coal, e.g. bituminous coal, have a poor capacity to absorb catalytic substances, particularly in watery solutions, even when ground. At times, coarse grained coals, such as brown coal, take on the catalyst only on their surface. In order to obtain a high degree of liquefaction of the carbonaceous substances in pressure hydrogenation, it is, however, desirable that the catalytic substance permeate the grains of coal as completely and uniformly as possible.

It has now been found that this disadvantage can be overcome by soaking the coal with a catalyst either fully or partly dissolved in a ketone or aldehyde.

Suitable catalysts may be metallic compounds of the 2. to the 8. group, particularly the 5. and 6. group, as well as compounds of cobalt, iron, tin and lead, and metalloids, such as chlorine, bromine, antimony, selenium or others, and their compounds. Among the metallic compounds, the halogenides, oxides, sulfur salts, thiocyanates, sulfides and phosphor compounds, are the best.

Suitable solvents for catalytic substances are acetone, acetylacetone, acetonylacetone, ethylpropylketone, cyclohexanane, acetophenone, as well as benzaldehide and phenylacetaldehyde. Ketonic acids, such as pyroracemic acid or levulinic acid, may also be used. Mixtures of these solvents with each other or with alcohols or low molecular fatty acids are also suitable.

One may, for example, dissolve the metallic chlorides of the iron group or the 6. group, particularly of molybdenum, or the thiocyanate of molybdenum, tungsten or iron, in acetone. Others may be dissolved in acetylacetone, such as cobalt chloride, iron chloride, cobalt-and molybdenum-thiocyanate, molybdenum halogenides and molybdic acid.

The feed stock, for example, is finely crushed or ground and sprayed with or soaked in a solution of the catalyst at ordinary or increased temperature and the solvent distilled off, if necessary.

At times, it may be of advantage to remove the alkalinic acting ash constituents in the coal, either fully or in part, or to neutralize them with acids.

The feed stock so prepared is then properly pasted with high boiling oil and subjected to pressure hydrogenation.

In the process under consideration the catalyst can be used thoroughly mixed with the coal, so that the yield in liquid products is very large and their quality very high.

Example.

Finely ground Ruhr bituminous coal, whose basic constituents have been neutralized with diluted sulfuric acid, is sprayed with acetone in which molybdic acid chloride, obtained by passing hydrogen chloride over slightly heated molybdic acid, is dissolved, in such a manner that 0.03% of the molybdic acid is absorbed by the coal. The coal is then dried and the evaporating acetone is recovered by condensation. The coal so prepared is then pasted with a heavy oil derived from the same coal in the proportion of 1:1 and treated, together with hydrogen, under a pressure of 250 atm. at a temperature of 460° C, whereby 95% of the carbon in the coal is converted to mainly liquid products containing 4.2% asphalt.

If 0.03% molybdic acid, together with hydrochloric acid ($MoO_3 + 2\ HCl$) is added, undissolved, to the coal, 94% of the carbon is converted to mainly liquid products, containing 6.5% asphalt, when operating under otherwise identical conditions.

Patent Claims.

Process for producing liquid hydrocarbons from coal in crushed and preferably pasted condition by treatment with hydrogen under pressure at increased temperature, whereby the feed stock is sprayed with a catalytically acting substance dissolved in whole or in part in an organic solvent, characterized by using ketones or aldehydes as solvents.

T-226

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

KCBraun
2-3-47

REPORT OF DISCUSSION ON A LET-DOWN HEAT EXCHANGE OF THE COAL STALL.

Blechhammer, 27 May, 1943.

I. Following the discussion in Ludwigshafen, 22 March 1943, Dir. Josenhans suggested to relieve the load on the preheater further by transmitting the heat contained in the letdown directly to the thick paste by a heat exchanger.

Dir. Josenhans suggested a heat exchanger consisting in principle of 2 parallel tubes welded together, wherein the letdown flows thru one tube and the thick paste with a little gas in the other, counter current. In the meantime Dir. Josenhans had already ordered corresponding devices to be made and the coefficient of heat transmission determined in tests with water and steam in both, double and quadruple, arrangements. The results obtained with the quadruple tube are considerably better than those with the twin tube. The calculations showed that in heating 26 tons of thick paste in heat exchange with 32 tons of letdown, a total length of 4000 m of 45 mm tube would be required. Dir. Josenhans reports the construction of such elements each 20 m long. Dir. Josenhans got in touch with Leuna about the welding and was told that the construction is feasible. The inside hollow spaces in the quadruple arrangement could be filled with cast metal, as zink, to improve the heat transmission. The difficulties of a flange connection is to be overcome by a sleeve, which, in addition, will have lower radiation losses. The linear expansion can also be controlled, according to Dir. Josenhans.

D. I. Franta suggests to transmit the excess heat contained in the letdown to a primary system by means of an auxiliary liquid and then transmit this heat to the coal paste in a secondary system. A suitable auxiliary liquid could not be found, as yet. The tubing required for D.I. Franta's scheme would be about the same as for Dir. Josenhans'.

II. Discussion.

1. Several years ago a block condenser, i.e. two parallel tubes surrounded by metal, was tested for its heat transmission. Results obtained indicated that, compared to a concentric arrangement of tubes, the K-values were much less, only

about 30-50%.

2. This spring Ludwigshafen made calculations and tests of the efficiency of parallel tubes variously arranged, among others, the arrangement suggested by Dir. Josenhans, in utilizing the heat contained in the letdown. The heating method primarily under consideration was gas. The results pretty closely check those obtained here, i.e. the K-value for a twin tube is about half that of a concentric tube, while with a triple tube arrangement the K-value is somewhat better.

3a.) Dir. Josenhans' arrangement to transmit the heat of the letdown to the thick paste was calculated in Ludwigshafen, see Appendix 1. On the assumption of using only two 70 mm high pressure tubes, a total length of 2400 m of these two tubes would be required, based on a thick paste thruput of 20 tons. A comparative calculation was also made of the auxiliary liquid scheme of D.I. Franta. For an installation of equal heat transmission a greater length of high pressure tubes is required with this scheme. Attention should be called to the radiation losses, which have been overlooked so far, but which are considerable, about 15%, because of the length of tubes.

3b). This arrangement produces a pressure loss of 15 atm. when using only 4000 m^3 gas. This increase in circulating pump differential pressure is difficult to take, because they are now almost loaded to capacity. Therefore, the make-up gas (Frischgas) would have to be supplied separately from the circulating system and at a higher pressure. In this connection Dr. Kimmerle points out that we would have to give up an important auxiliary medium for evaluating the stalls, i.e. the density differential in the stall.

3c). A number of charts were submitted showing the irregular accumulation of the letdown at Gelsenberg, including:

1. The chart of the liquid level gages.
2. The chart of the cold gas ~~gage~~ meter for Converter 3.
3. The chart of the mean value recorder, showing the momentary yield of letdown.
4. A temperature chart from the thermoelements attached to the high pressure line, which also indicate the irregular yield of letdown.

It may happen that the letdown valve is completely closed for from 5 to 8 minutes, during which time no letdown accumulates.

This happens mainly when the converter contents have been reduced in volume after a marked decrease in cold gas and no product reaches the catch pot. Appendix 2 shows how the temperature of the cold paste drops at the outlet from the letdown heat , exchanger in this case and that this drop is still apparent at the inlet to the first converters to the extent of 10-15°C. These fluctuations are difficult to take because the installation of a fifth converter has been decided on, which is to run with a starting temperature as low as possible.

3d.) Difficulties may also be expected with the parallel arrangement of the thick paste, but particularly with the letdown. A uniform operation of the two needle valves is necessary to obtain a uniform heating up of the coal paste.

3e.) The starting up of a stall, with its heavily fluctuating yield of letdown, would probably also cause difficulties in heating up. Neither does it appear simple to empty such a long heat exchanger system without trouble in shutting down a stall. Arranging the quadruple tubes over 1000 m long near the stall will cause great difficulties.

4.) Ludwigshafen makes a counter proposal to recover the heat contained in the letdown. This proposal is based primarily on a heat exchange experiment successfully conducted at Gelsenberg. For relieving the preheater at Gelsenberg the entire coal paste with the entire gas volume is run thru a paste heat exchanger wherein this paste with a mean concentration of 46% is heated without difficulty from 100° to 305° C. This experiment has now been running for 5 weeks and the K-value has been steady at about 210. It has also been known from previous experiments at Ludwigshafen that bituminous coal paste, at least of normal concentration, could be heated without hesitation to the lower limit of the swelling range, about 300°C. It is, therefore, proposed to heat up thick paste plus paste gas instead of gas to about 250° C in the gas heat exchanger (H.E.4) proposed at the last meeting. On the contrary, the entire inlet gas is to be heat exchanged with the letdown:

a.) Either in a normal double coil (jacketed tube) made by Mannesmann, see Appendix 3, or

b.) in a specially constructed heat exchanger element.

In a.) the letdown would flow in the inner circular cross-section and the gas in counter current in the outer concentric ring space. The entire gas could hereby be heated from 30° to about 280° C and this gas would be added partly to the thin paste and partly to the thick paste. The objection made by Upper Silesia that water cooled valves would be necessary for the gas distribution is over-ruled by Ludwigshafen, though it is admitted that at least in starting up a stall the thick paste stream should run without gas, or better yet, that only the inlet gas to the thin paste should be heat exchanged. Since a value of 500 from the letdown and one of at least 1500 for hydrogen can be figured, the gas heat exchange with the let-down will give a K-value of at least 400, compared to the apparatus proposed by Dir. Josenhans, for which a K-value of only about 125 could be obtained. This arrangement of the gas heat exchanger would also permit an appreciably greater temperature difference, since the gas enters @ 30° and an extreme heating of the gas can be dispensed with, so that a length of only about 12% of that required by Dir. Josenhans' scheme would be required.

III. It was decided to develop both schemes, that suggested by Dir. Josenhans as well as that proposed by Ludwigshafen, to the point of practical maturity. The Ludwigshafen proposal is to be given precedence, because it may be applied in practice with lesser and known media and greater operating simplicity. The scheme of exchanging the heat with an auxiliary liquid may also be further developed, if a suitable medium is found for transmitting the heat. The Ludwigshafen proposal has two unknown factors:

a). Can 52% thick paste be heat exchanged? In this case the concentration of the thin paste, as well as the thick paste, may be lowered at the expense of a greater thick paste thruput.

b). Is there assurance that the construction of double tube heat exchangers is possible?

Our immediate program is therefor:

1). Ludwigshafen to measure viscosities of thick paste within the range of 46 to 53% and the temperature range between 100 and 300°C. These viscosity measurements are to be made with a specially constructed viscosimeter under pressure and without pressure, as well as with the apparatus operated by Dr. Hupfer for determining the heat transmission.

2). After making these experiments, Gelsenberg shall also be advised of the results, so that, in case of favorable results, Gelsenberg may possibly decide to increase their present concentration of 46%.

3). A meeting for the mutual exchange of experiences shall be held with the interested plants at a suitable time, in which all questions affecting this problem shall again be discussed. An experiment with a heat exchanger with tubes of larger cross-section, 30 mm dia. proposed by Ludwigshafen, is also to be initiated then.

Appendix 1. -- Ludwigshafen, 19 May, 1943.

Re:--Let-Down Heat Exchanger.

Four cases of a let-down heat exchanger for Upper Silesia conditions are calculated herein.

1). The thick paste is heated in a heat exchanger consisting of 2 parallel tubes, 70 mm dia., welded together, as proposed by Dir. Josenhans.

2). An auxiliary liquid flowing in a jacket surrounding the high pressure tube. The heat of the let-down is first absorbed by this liquid (oil) and is then transmitted to the paste in a similar second system. Table 2 shows the alpha values calculated for Dinyl. Dinyl, accordingly, is eliminated as an auxiliary liquid. It has not been determined yet what liquid would give the high value of alpha = 500, used in Table 1.

3). The same case as 2), except that the letdown is cooled more, to 262°C, for direct compar~~ed~~ison with Case 1). The coal paste is heated correspondingly higher.

4). Supplementing Cases 1 to 3, Dr. Wilde calculated a 4th case on the same basis:

It was assumed to be possible to separate the paste and letdown stream into 2 parts (different presses and 2 expansion nozzles). The result indicates 2 tubes on the charging side and 2 tubes on the return side, each 48/76 mm, arranged diametrically opposed to each other and wall to wall. A heating tube is wrapped tightly around the 4-tube bundle. The space between the tubes is filled with lead or cast aluminum.

In consideration of the radiation losses it may be remarked that 200,000 Kcal/h were supplied in each case. In reality, the radiation losses are probably considerably greater.

α-Value for Coal Paste on Wall at Temperatures 100 to 300°C.

For the method proposed by Dir. Josenhans, in which the hot letdown is to transfer its heat to the thick paste, an α-value of 500 kcal/m²/°C/h for the letdown was determined from several measurements.

The value for the paste was determined from operating measurements, taken from the cold pass in the temperature range between 100 and 300° C.

The α-value for paste on wall:

in Gelsenberg for new tubes	= 264
in Gelsenberg for old tubes with a load of 23 t paste and 3000 m³ gas.	= 204
In Pölitz after abt. 200 operating days with a load of 20 t paste and 4000 m³ gas.	= 217
In Scholven after abt. 250 operating days with a load of 28 t paste and 2000 m³ gas.	= 220

If an α-value of 250 for the thick paste is used in the calculations for the letdown cooler, this would probably represent the upper limit, inasmuch as in the 3 plants mentioned only Pölitz runs thick paste with a value of about 220. Gelsenberg and Scholven run only paste of normal concentration thru this part.

Table 1. Let-Down Cooler

Tube Dimensions		2 Tubes 70 mm	Jacket Tubes 70/102-137/146	
Case		1	2 (With aux. liquid)	
Heat Exchanger, Charging Side	t/h m^3/h	20 (Paste) 4000 (Gas) x)	20 (Oil Paste) 4000 (Gas)	20 (Oil) --
Heat value	Kcal/°C	11 920	11 920	12 000
α-value	Kcal/°C,h,m^2	300	300	500
Weight (total)	t/h	21	21	20
Volume	m^3/h	22 + 12.3 = 34.3	34.3	22
Spec. Grav.	kg/m^3	615	615	900
Velocity	m/s	2.47	2.47	1.58
Δ p/m tube	atm.	0.0107		
H.E. (Return)	t/h	32 (Letdown)	20 (oil)	32 (Letdown)
Heat value	Kcal/°C	18 550	12 000	18 550
α-value	Kcal/°C,m^2,h	400	500	400
Weight	t/h	32	20	32
Volume	m^3/h	35.5	22	35.5
Spec. Grav.	Kg/m^3	900	900	900
Velocity	m/s	2.55	1.58	2.55
Δp/m tube	atm.	0.0167		
Temperature	°C	262 <- 420 100 -> 330	170 <- 340 100 -> 255	300 <- 420 170 -> 340
Δ t	°C	122	77	103
Heat transmitted	10^3 Cal/h	2 740	1 840	2 040
Radiation	"	200	200	200
K-value	Kcal/°C,h,m^2	147 , 0,60 = 87	160	180
Surface	m^2	260	150	112
Tube length	m	1 200	700	510
Δ p Charging xx)	atm	15		
Δ p Return	atm	23		

xx) - 15 % for Stall

x) at 8000 m^3/h Gas Δ p is abt. 50 % greater.

Table 1. Let-Down Cooler (Continued)

Tube Dimensions		Jacket Tubes 70/102-137/146		2 x 2 Tubes 48/76 ø
Case		3(with aux.liquid		4 (Lead as aux. liquid).
Heat Exchanger, Charging Side	t/h m^3/h	20 (Paste) 4000 (Gas)	27 (Oil) --	20 (Paste) 4000 (Gas)
Heat valve	Kcal/°C	11 920	16 200	11 920
α-value	Kcal/°C,h,m^2	300	500	300
Weight (total)	t/h	21	27	21
Volume	m^3/h	34.3	30	34.3
Spec. Grav.	kg/m^3	615	900	615
Velocity	m/s	2.47	2.17	2.63
Δp/m tube	atm.			0.0177
H. E. (Return)	t/h	27 (Oil)	32 (Letdown)	32 (Letdown)
Heat valve	Kcal/°C	16 200	18 550	18 550
α-value	Kcal/°C,m^2,h	500	400	400
Weight	t/h	27	32	32
Volume	m^3/h	30	35.5	35.5
Spec. Grav.	Kg/m^3	900	900	900
Velocity	m/s	2.17	2.55	2.73
Δp/m tube	atm.	0.0121	0.0167	0.0280
Temperature	°C	180 <- 350 100 -> 315	262 <- 420 180 -> 350	262 <- 420 100 -> 330
Δt	°C	54	76	122
Heat transmitted	10^3 Cal/h	2 550	2 750	2740
Radiation	"	200	200	200 .
K-value	Kcal/°C,h,m^2	160	180	161 . 0.85 = 137
Surface	m^2	300	200	165 Charg.+165 Ret
Tube length	m	1 370	930	2 x 550 Charg. + 2 x 550 Ret.
Δp Charging xx)	atm.			115
Δp Return	atm.			18

xx) + 15 % for Stall

179

Table 2. T-226

CALCULATION OF COEFF. OF HEAT TRANSMISSION BETW. DINYL & TUBE

$$\frac{\alpha \cdot d}{\lambda} = 0.024 \cdot \left(\frac{w \cdot d \cdot \gamma}{\eta \cdot g}\right)^{0.8} \cdot \left(\frac{\eta \cdot g \cdot c}{\lambda'}\right)^{0.37}$$

For jacket tubes 70/102 - 137/146 the free

Cross-section $F = 0.00657$ m^2;

For 20 m^3/h Dinyl the velocity $w = 0.85$ m/s.

$d = 0.137 - 0.102 = 0.035$ m

$\lambda = 0.117$ Kcal/°C, m, h

$\lambda' = 0.117/3600 = 0.325 . 10^{-4}$ Kcal/°C, m, s

$\gamma = 900$ kg/m^3 } for 200 °C

$c = 0.55$ Kcal/kg, °C

$\eta = 40 . 10^{-6}$ kg . s /m^2

$$\alpha = \frac{0.117}{0.035} \cdot 0.024 \cdot \left(\frac{0.85 . 0.035 . 900}{40 . 10^{-6} . 10}\right)^{0.8} \left(\frac{40 . 10^{-6} . 10 . 0.55}{0.325 \times 10^{-4}}\right)^{0.37}$$

$$= 0.08 \cdot 6700^{0.8} \cdot 6.8^{0.37}$$

$$= 0.08 \cdot 1150 \cdot 2.3 = 187$$ Kcal/°C, m^2, h.

Appendix 2.

Re: Let-Down Heat Exchanger.

According to the proposal of Dir. Josenhans a part of the coal paste is to be heated in a heat exchanger by the letdown withdrawn. With the operating method proposed for Upper Silesia the thick paste, 20 t/h, is to be heated to about 330°C. A connection between the injection side and the letdown side is being made here for the first time.

Since, under certain conditions, it may be possible that no letdown will be withdrawn for a short period, Dr. Wilde calculated for conditions in Upper Silesia how far the outlet temperature of the thick paste drops if the letdown stops but the paste presses keep on running. The curves indicate that:

After 4 minutes the paste temperature drops 135° C, corresponding to 1.6 x 10^6 kcal/h, which equals about 28° C based on the total thruput. The preheater now works with a greater, i.e. more favorable, temperature difference and regains about 10-12° of it, so that the total paste enters the first converter with a temperature still more than 15° lower. If a fifth converter is to be introduced in Upper Silesia as a preheat converter requiring the lowest possible reaction temperature, fluctuations of 7-10° C should be avoided.

Appendix 3.

Leuna, 24 May, 1943

To: I.G. Farbenindustrie, A.G.
Ludwigshafen, Rh.

Re: Your letter of 15 May, 1943, regarding exchange of experiences with letdown-paste heat exchanger.

In Leuna, too, the letdown is not produced constantly. Since this causes fluctuating quantities of heat, the heated gas is injected into the paste-gas mixture ahead of H.E.II, so that H.E. II will act as equalizer and protect the converter from fluctuations.

Your questions are answered individually as follows:

1). The fluctuations in the letdown yield, which is recorded every half hour, equals ± 3% in quiet operation, with a mean value of 7000 l/h.

2). These fluctuations occur constantly.

3). These fluctuations in letdown quantity are recorded as temperature fluctuations by 2 welded-on thermoelements. The letdown quantity is also measured by an Eckardt meter, which is read and recorded every half hour.

4). If the converter temperature rises above normal, or if the coal paste injection pumps are down, there will be no letdown for up to 15 minutes.

5). Normally, there is a regular alternation between a letdown flow of 30 seconds duration and a pause of 1-2 minutes, caused by the automatic operation of the letdown valve.

6). In starting up a stall, which is done with 8000 L/h pasting oil, about 7000 L/h enter the hot catchpot when the feed is changed to coal paste. After the change to coal paste, which is gradually increased from 8000 L/h to the desired maximum of 32000 L/h, the converter temperatures are adjusted so that the letdown produced equals between 25 and 30% of the coal paste injection at the time. In a condition of equilibrium, i.e. after the stall has been brought up to reaction temperature, the quantity of letdown equals only 22-25% of the injection, or 7000-8000 L/h letdown with 32000 L/h coal paste injection.

7). No, because the irregular quantities of heat supplied will be equalized in a following heat exchanger (coal paste-product vapors-gas mixture) and a final preheater (Spitzenvorheizer).

The same questions, not available, are answered by Pölitz, 24 May, 1943:

1) and 2). The quantity of let-down in coal stalls fluctuates up to 3 m^3, and the temperature, recorded by clamped-on thermoelements, up to 1.5 mv. In tar stalls, the letdown quantity fluctuates up to 4 m^3 and the temperature up to 3 mv. These small fluctuations occur regularly.

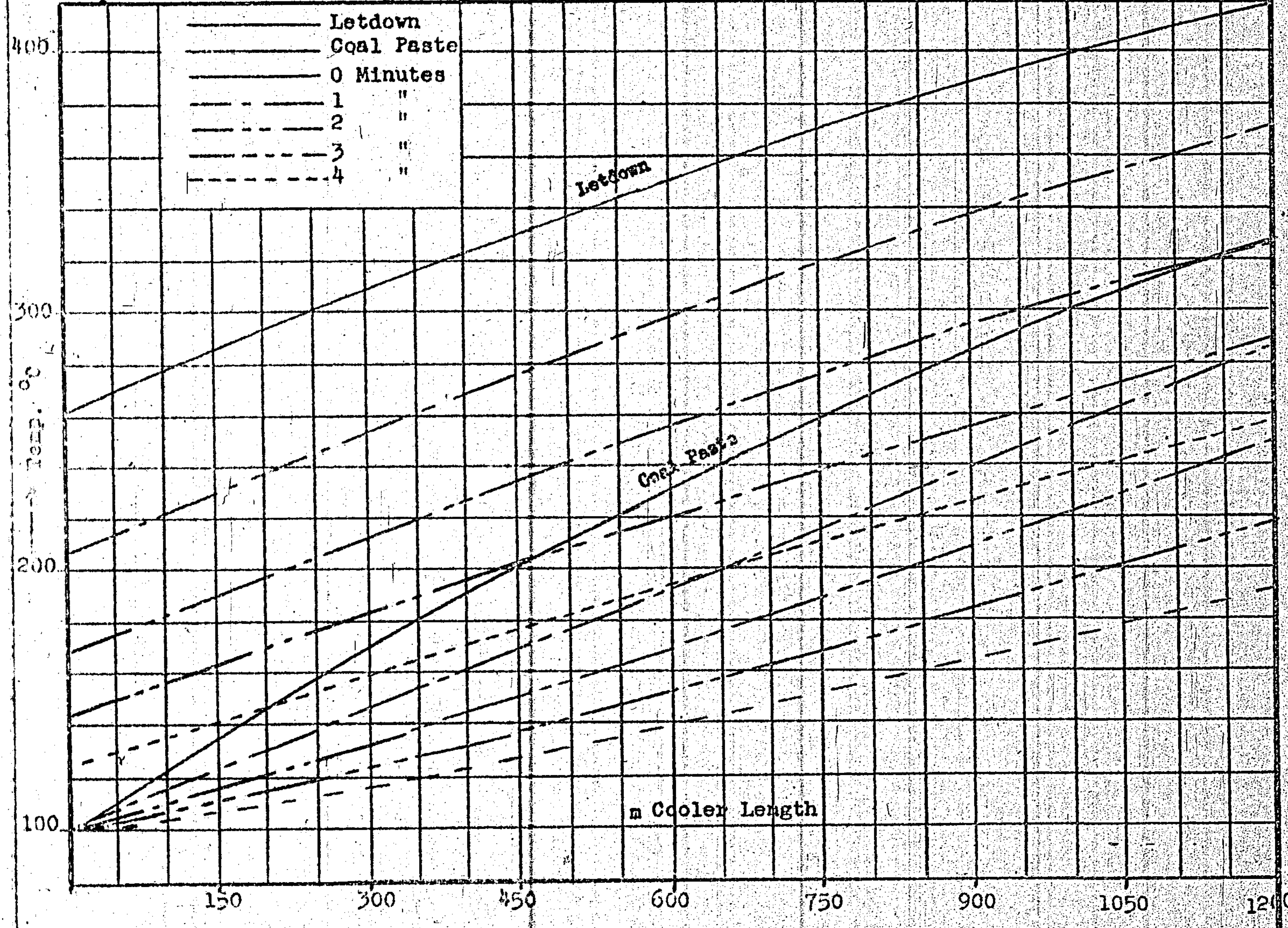
3). The fluctuations are recorded by elements and mean value recorders.

4). and 5). In fluctuations in the hot catch pot level of tar stalls it may happen that no letdown is drawn off for 5-10 minutes and at times only half the normal amount for almost an hour. No such strong fluctuations occur, in general, in coal stalls as in tar stalls, i.e. there is a constant flow of letdown, even with a temporarily lower level in the catchpot.

6). When changing from pasting oil to coal paste, up to 5 m^3/h of letdown is produced. After about 6 hours equilibrium is reached.

7). We have no reason to expect operating difficulties in heating paste by letdown.

Temperature Curves of Stagnating H.O.L.D. After 0-4 Minutes in Letdown-Paste Heat Exchanger



DOUBLE TUBE COOLER, NOM PRESS. 700 ATM.

SUBSTITUTE FOR DOUBLE COIL COOLER N.P. 700 ATM.

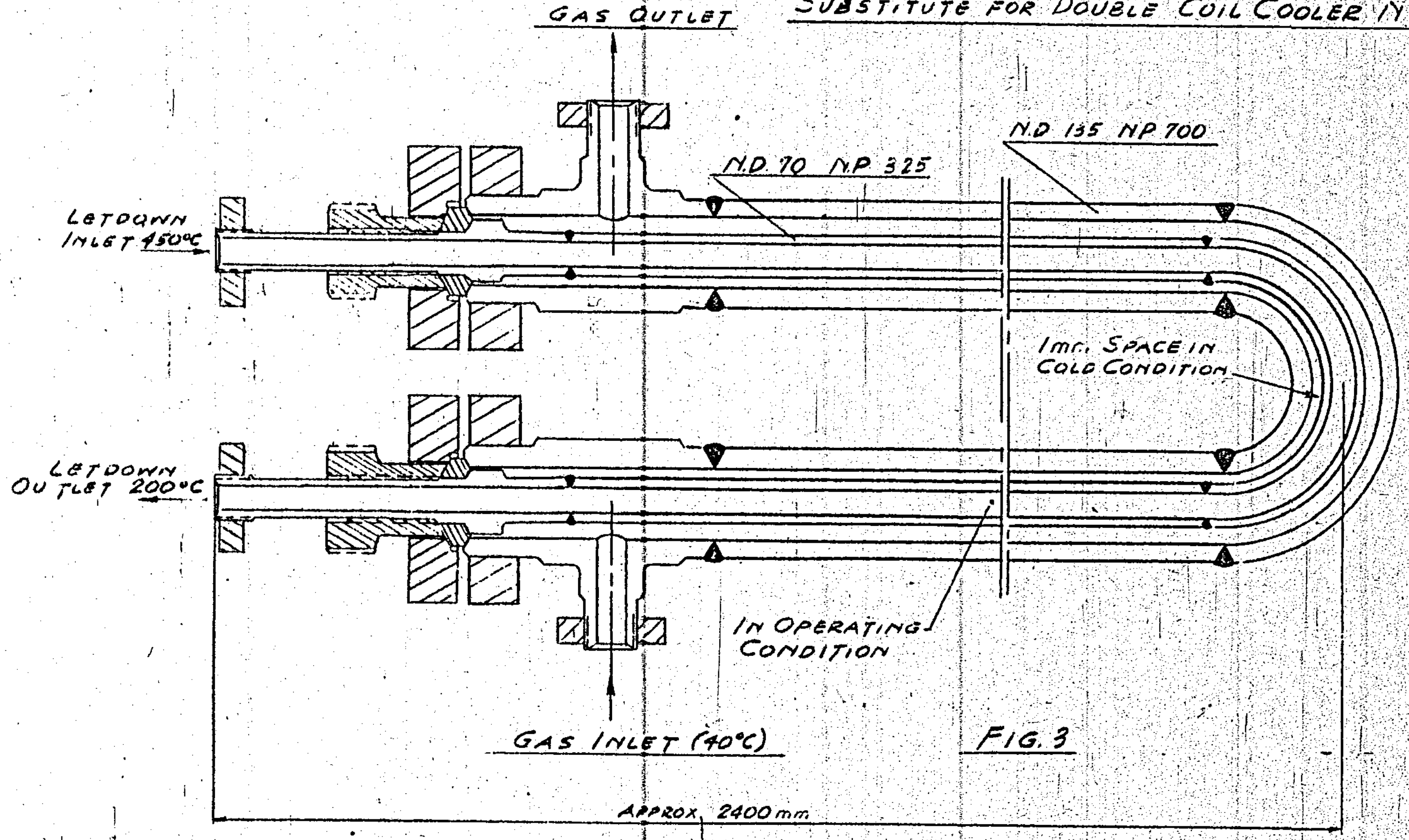
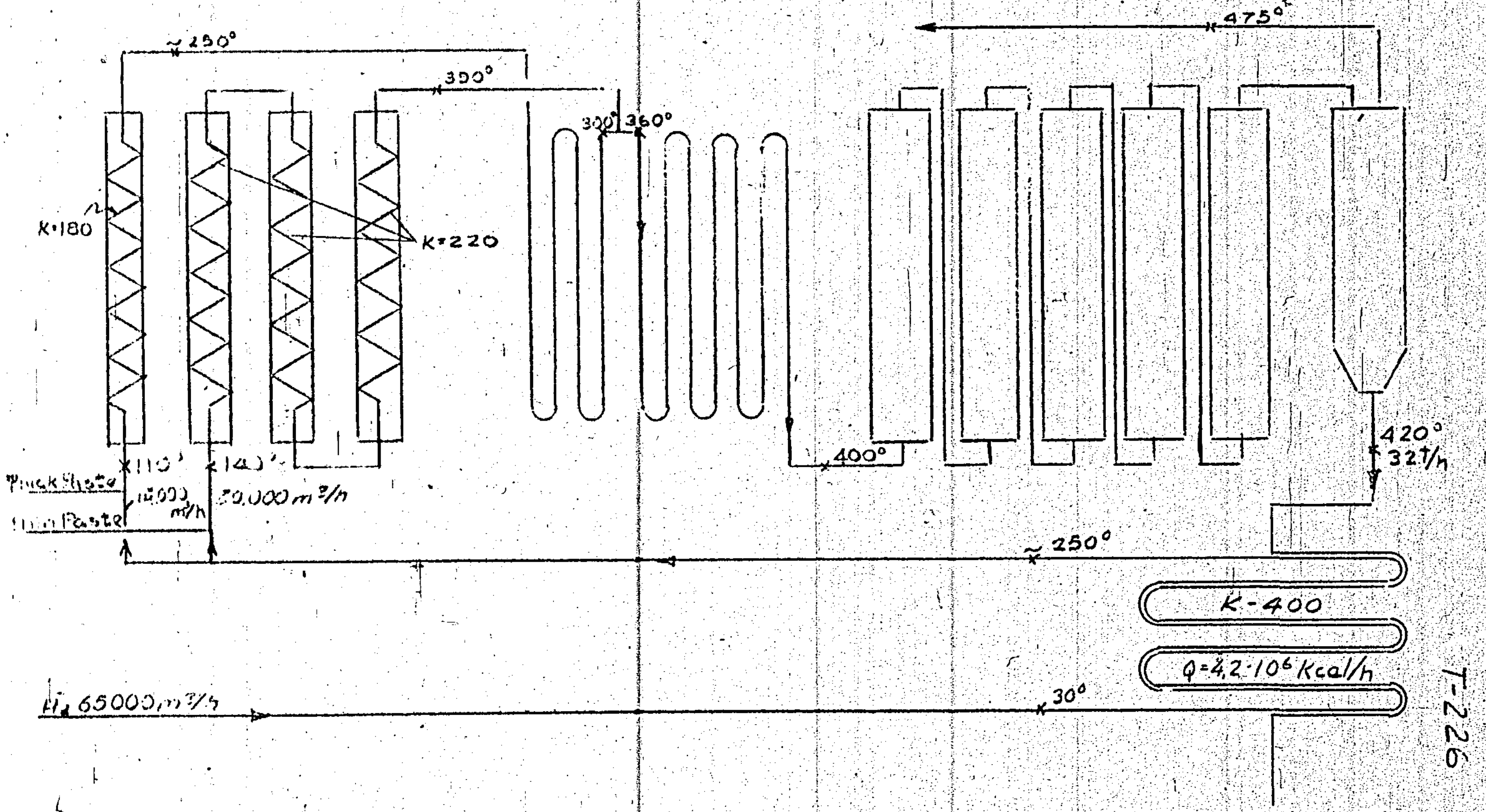


FIG. 3

T-226
App. III.

APPENDIX 4.

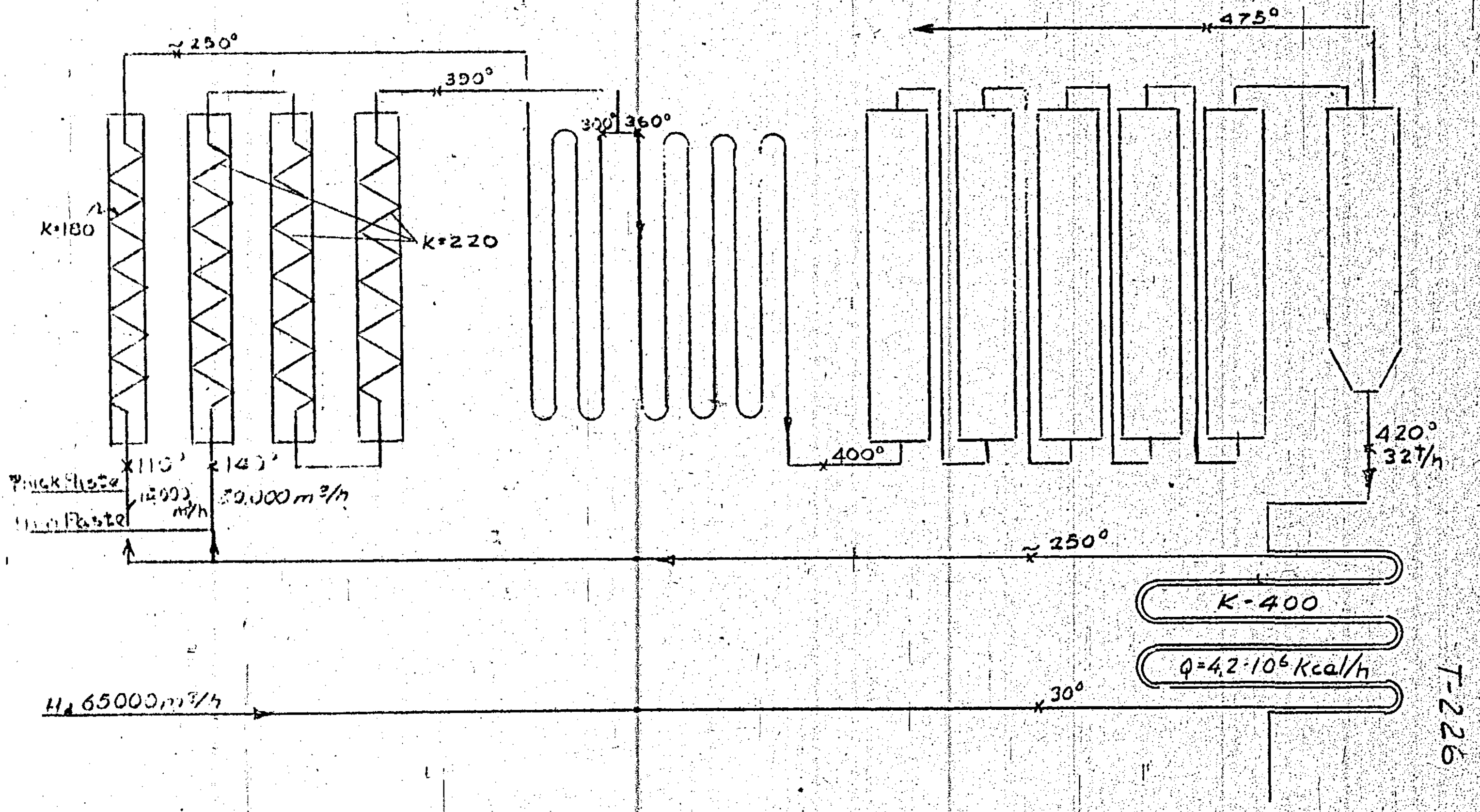
LUDWIGSHAFEN PROPOSAL FOR RECOVERY OF HEAT FROM THE LET-DOWN



T-226

APPENDIX 4

LUDWIGSHAFEN PROPOSAL FOR RECOVERY OF HEAT FROM THE LET-DOWN



T-226

188

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

T-227

KCBraun
2-4-47

PROCESS FOR THE PRESSURE HYDROGENATION OF CARBONACEOUS SUBSTANCES.

German Patent 716470
(Supplement to Patent 713792)

Class 12o, Group $1o_5$
March 5, 1931

Issued to

Deutsche Gold & Silber Scheideanstalt,

Frankfurt, a.M.

D.R.P. 716470

It is already known that the pressure hydrogenation of carbonaceous substances in the presence of Mo or W or their compounds, may be conducted in such a way that the presence of 1 to 12% H_2S, based on the substance to be hydrogenated, in the hydrogenation vessel may be assured, and that for every substance to be hydrogenated a definite optimum H_2S-concentration is used. In particular, it is known that benzol and its homologs may be produced by pressure hydrogenation from naphthalene by this process, in which temperatures above the point of temperature recession are used. The suggestion to recirculate the gas stream in this process has already been made, wherein the quantity of naphthalene and of hydrogen and the optimum quantity of hydrogen-sulfide is kept as constant as possible.

The main patent protects a process for the adjustment of the maximum increase in effectiveness of iron, cobalt and/or nickel catalysts in relation to the yield in the desired products of reaction in the pressure hydrogenation of carbonaceous substances, particularly tars or oils, in the presence of sulfur, by a change in operating conditions. This process is characterized by changing the H_2S-concentration within the range of 1 to 15% by weight of the substance to be hydrogenated until the maximum effectiveness has been reached.

According to the invention at hand the process of the main patent is conducted in such a way that a gaseous portion of the products of hydrogenation, containing the optimum quantity of H_2S required for the process, is separated from them and used again for hydrogenation in the recirculating system.

In working this process one may, e.g. proceed in such a manner that the liquid and gaseous products of hydrogenation are partially decompressed and the hydrogen-rich "A" off-gas obtained thereby is returned to the hydrogenation vessel with such an H_2S content that this, together with H_2S generated from the sulfur content of the feed stock, will equal the optimum quantity of H_2S required for the process. It has been shown that it is possible herewith to adjust the H_2S content of the hydrogenation gas in the recirculating system, by the proper choice of the expansion pressure and temperature, to the desired degree, without disturbing side effects, such as a troublesome accumulation of methane and other hydrocarbons in the hydrogenation vessel. By completely expanding the residual products of hydrogenation to atmospheric pressure, a "B"-gas rich in hydrocarbons is released, which still contains a large amount of H_2S. In case the H_2S in the "A"-gas is not enough, additional H_2S may be separated from the "B"-gas and added to the "A"-gas in the desired amount.

According to another operating method of this invention, the product of hydrogenation is decomposed into a liquid and a gaseous portion, while maintaining, or nearly maintaining, the operating pressure. The gaseous portion consists largely of hydrogen and is returned to the reaction vessel, together with such quantities of H_2S that the desired concentration of H_2S is maintained in the vessel.

Only unimportant differences in pressure must be overcome with this operating method. Consequently, simple apparatus can be used, which permit moderate increases in pressure, if need be, in order to reinstate the operating pressure. In processing materials rich in sulfur, the off-gas may contain so much H_2S that, if the gas is returned in this condition, it would cause an accumulation of H_2S above the optimum concentration. In such cases, either the excess H_2S or all of it is removed, in which latter case the H_2S necessary to increased effectiveness is again added to the gas.

Oils, poor in sulfur, which are to be hydrogenated themselves, may be advantageously used for washing the H_2S out of the circulating hydrogenation gas, and at the same time adjusted to the desired sulfur content.

One may, e.g. completely or largely wash out the H_2S from only a portion of the H_2-rich off-gases of the hydrogenation process and then adjust the H_2S content of the gas returned to the reaction vessel to the desired degree by adding washed gas to the unwashed gas.

Under certain conditions the adjustment of the optimum H_2S content may also be obtained by discharging a certain quantity of the off-gas containing H_2S thru a valve and replacing the discharged gas by a corresponding quantity of hydrogen. One may also combine both methods, that of removing a portion of the hydrogenation gases with that of removing desired amounts of H_2S.

In cases where the H_2S content of the off-gases containing hydrogen is insufficient to assure optimum increase in effectiveness, additional H_2S must be provided or such quantities of H_2S, sulfur or other sulfur compounds supplying H_2S must be added to the material to be hydrogenated, in order to assure the desired H_2S-concentration in the reaction vessel.

In all operating methods of this invention the H_2S is preferably added to the recirculating gas stream only after the gas stream has passed the conveying device, pumps, etc, i.e. just before the return of the gas to the hydrogenation vessel. The required H_2S can also be added here to the make-up hydrogen. If, e.g. the H_2S-content of the recirculating gas is just enough to assure optimum H_2S concentration in the hydrogenation vessel, the

H_2S may first be removed as completely as possible just before the conveying device, e.g. by washing processes, while maintaining the pressure, and then add it again to the circulating system in the desired amount behind this device. Such a by-pass of the H_2S around the conveying device will prevent corrosion of this device.

One may, e.g. also proceed in such a manner that the gas-vapor mixture leaving the hydrogenation vessel is passed thru cooling devices and then into a scrubbing tower, in which water under pressure flows against the mixture from the top, so that the scrubbing tower acts as a spray cooler at the same time. The run-off mixture of watery liquid and oily condensate is separated, the watery layer, which contains ammonium-sulfide and most of the H_2S in solution and is still under the same pressure existing in the reaction vessel, is conveyed to an injector (Montejusanlage), which by means of compressed hydrogen, e.g. conveys the watery liquid to a second scrubbing tower. Here, the circulating gas, practically completely freed of H_2S in a secondary washer with the aid of alkalinic liquids, if need be, enters at the bottom after it has been compressed to the necessary working pressure by a circulating pump. The gas is charged with the required quantity of H_2S in the second washer, by bringing it into intimate contact with the washing liquor containing H_2S from the first tower. The reabsorption of H_2S may be facilitated by heating. The mixture of hydrogenation gas and H_2S may be directly conveyed to the reaction vessel from the second tower.

The condensates obtained from condensation under pressure may also serve as a source of additional H_2S. The H_2S may properly be obtained from these by treatment with washing liquid and subsequent separation by heating, for example. But, as already mentioned, the additional H_2S may be obtained from the "B"-gas fraction obtained in the expansion of the condensate.

It is already known that the hydrogenation gases emerging from the hydrogenation vessel may be freed of the hydrocarbons and sulfur compounds, particularly H_2S by scrubbing with oils. According to this older process, the gas so washed and used again for renewed hydrogenation contains less than 0.3% H_2S. On the contrary, according to the invention at hand, the H_2S-content is only reduced to a concentration which will produce increased effectiveness in the iron, cobalt and/or nickel catalysts used, and which amounts to over 1% in all cases. According to another working method of the process at hand, the H_2S is completely removed by the scrubbing process ahead of the conveying device and certain quantities of H_2S, which will produce increased effectiveness, are then again added to the hydrogenation gas after passing the conveying device. The hydrogenation gas returned to the hydrogenation vessel contains not less than 1% H_2S.

The hydrogenation process is preferably effected at pressures above 100 atm., and temperatures between 400 and 600° C. The H_2S-concentrations required for increased effectiveness generally equals between 1 and 15% of the feed stock. The most effective concentration within these limits can readily be determined by experiment. This may be done, e.g. by first determining the operating conditions best suited for the material to be hydrogenated (free of sulfur or with its natural sulfur content), in view of the desired product of hydrogenation, such as gasoline or middle oil, when using the desired iron, cobalt and/or nickel catalyst. After this has been done, the conditions are determined, by which the best yield in the desired end product is obtained by the combined effect of H_2S and catalyst, by varying the H_2S-concentration in the hydrogenation vessel. The term "end product" here does not designate the immediate raw product of hydrogenation, but the refined industrial products obtained from these. By correctly adjusting the H_2S concentration in the hydrogenation vessel, not only can the yield itself be increased, but purer products can be obtained, which, in the subsequent refining process, will suffer only small losses by the removal of desired by-products, or which, in certain cases, may even be obtained in such a pure form that they will not need to be refined.

Example 1.

A brown coal tar middle oil with a specific gravity of 0.979 and a sulfur content of 0.9% is hydrogenated at 200 atm. in the presence of a nickel-hydroxide catalyst in a stream of hydrogen in such a way that 1560 liters of hydrogenation gas is used for each kg. of oil. The reaction is started with the addition of 2% sulfur to the middle oil. The products of reaction are expanded to 100 atm. and cooled. For each kg. oil used, there escape 970 liters of "A"-gas, based on 760 mm and 0°C, containing about 83% H_2, 12.5% hydrocarbons and 21.8 mg H_2S/l. This gas is recompressed to 200 atm. and again conveyed to hydrogenation after adding 590 liters of make-up gas. In the further expansion to atmospheric pressure an additional 87 liters of "B"-gas are obtained, which contain 13% H_2, 97% methane hydro-carbons, and 90 mg H_2S/l.

The product of reaction obtained is a clear oil with a specific gravity of 0.842, which contains 58% constituents boiling to 180°, no phenols and hardly any unsaturated hydrocarbons.

If the same brown coal tar middle oil is hydrogenated under the same conditions, but without returning the "A"-gas to the process and using 1560 liters of make-up H_2 per kg. of feed stock, instead, a hydrogenation product is obtained with a specific gravity of 0.858, containing 5% phenols, 11% unsaturated hydrocarbons, and only 50% of constituents boiling to 180° C.

Example 2.

Crude mineral oil with a specific gravity of 0.868 and 2.6% sulfur content hydrogenated at 200 atm. hydrogen pressure and 450 to 560°C. The catalyst used is cobalt-hydroxide. Preliminary tests indicated that for optimum effectiveness of the cobalt catalyst, this mineral oil must contain 6% H_2S, based on the crude oil.

The hydrogenation is generally so conducted that 1780 liters hydrogenation gas is used per kg. oil. After hydrogenation is started by adding 3% sulfur to the mineral oil and after condensing the products of reaction at 200 atm. pressure there escaped 1335 liters of a gas containing 95.8% hydrogen, 2% methane, and 30 mg H_2S/1.

37.8 g of sulfur per kg. of oil is, therefore, recovered from this off-gas. In order to maintain the optimum, however, only 30 g of sulfur are required. 335 liters are separated from the 1335 l off-gas and freed of H_2S by means of alkalinic iron-hydroxide suspension. The gas so freed of H_2S, together with 445 l make-up H_2 and 1000 l of unwashed off-gas containing H_2S, is returned to the reaction vessel. In the expansion of the liquid condensates, there escape another 113 l of gas containing 59% methane hydrocarbons, 35% H_2, and 160 mg H_2S/1.

With this operating method, 81.5% of a clear oil with a specific gravity of 0.760 is obtained. The gasoline yield equals 56% of the feed material. If we operate without the addition of sulfur, with make-up gas only, the oil yield is 74% and the yield in gasoline only 48%.

If the circulating system is operated without reducing the H_2S-content of the added off-gases to the required amount, the off gas is rapidly enriched with H_2S and the gasoline yield drops to 40%.

Patent Claims.

1. Process for the adjustment of the greatest increase in effectiveness of iron, cobalt and/or nickel catalyst, in relation to the yield in the desired products of reaction in the pressure hydrogenation of carbonaceous substances in the presence of sulfur, by variations of the operating conditions according to patent 713792, characterized by separating a gaseous portion of the products of hydrogenation (if need be by partial expansion)

containing the optimum quantity of H_2S required for the process as well as the residual hydrogen and returning it to hydrogenation in the circulating system.

2. Process according to Claim 1, characterized by freeing the gaseous portion of the products of hydrogenation completely or largely of H_2S before its entry into the conveying device and then mixing it with the optimum quantity of H_2S behind the conveying device.

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

T-228

KCBraun
2-5-47

TEST OF 120 mm THREADED FLANGE FOR 325 ATM.
(Measurement of Deformation)

Leuna Werke, 11 March, 1941

Problem:

A 90 mm threaded flange of 81 had been tested for 325 atm. (Test #15/510). This flange split into 3 pieces when it was drawn tight. The reason were old cracks, of which one extended from the outer side to a bolt hole. This raised the question what change in stress distribution and what increase in stress is caused by such a defect in the flange?

Result:

The distribution and extent of the deformations on the outer surface of a normal 120 mm. 325 atm. threaded flange was measured. Then a bolt hole was slit from the outside and the deformation on the inside of the slit hole was measured, using a sensitive Askania gauge.

The test arrangement may be recognized on the attached sketches. Sk-1 shows the measured deformations as a measure of strain or effort, SK-2 shows the stresses calculated from them. They are indicated on the outline of the surface, outside of the section where positive, inside of the section where negative. The second measurement with a slit bolt hole is shown in red (at right).

For test purposes the load was applied in a direction opposite to that used in practice, which, however, does not affect the distribution and extent of the deformations.

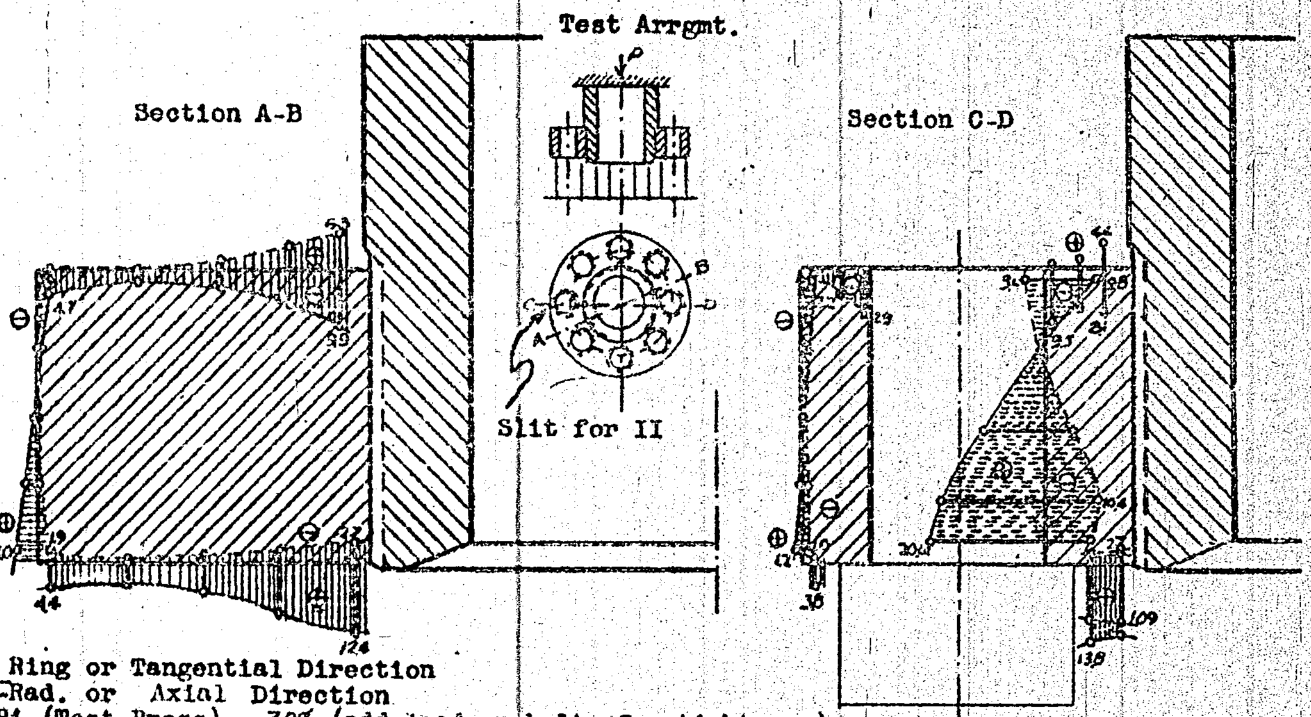
With a normal flange, black lines, the strains and stresses differ very little from each other. The signs and distribution in the ring test are evident on the top compared to the bottom side.

The signs in the radial direction would be expected to be just the opposite, if we conceive the flange assuming a bell shape due to bending. However, according to the measurements it must be assumed that the transformation into the bell shape is caused principally by transverse forces. The compressive stresses caused thereby on the inside of the flange, whose main direction is unknown and which cannot be measured either, then cause the measured deformations and unexpected signs.

The maximum load on the flange was chosen to be 80 tons, at which positive tightness may be assured, assuming all bolts drawn uniformly tight. However, from observation in practice we may assume that in reality the bolts are drawn tighter and irregular, particularly on smaller flanges, as the 90 mm. It seems, therefore, quite within the range of possibility that double the stresses found in this test may occur in practice.

Fundamentally, the greatest stress may be expected to occur on the inner (threaded) edge, according to the test. (Increased stresses due to the threads are not brought out in this test). When the outer material around a bolt hole is removed the maximum stress is shifted to the inner edge of the hole. It is 50% greater than in a normal flange. (Here also, the increase in stress directly on the sharp edge is not brought out by the test). Since there exists a compressive stress on this edge, in addition and perpendicular to the high tensile stress in an axial direction, it may be assumed that sliding is not obstructed here, and that not the shearing strength but the elastic limit of the material must be considered the limit of overstrain, insofar as the design stress is not shifted in another direction by the shape of the flange and the condition of the material.

In any case, a break in the outer flange material at the bolt hole must be considered as seriously endangering the flange.



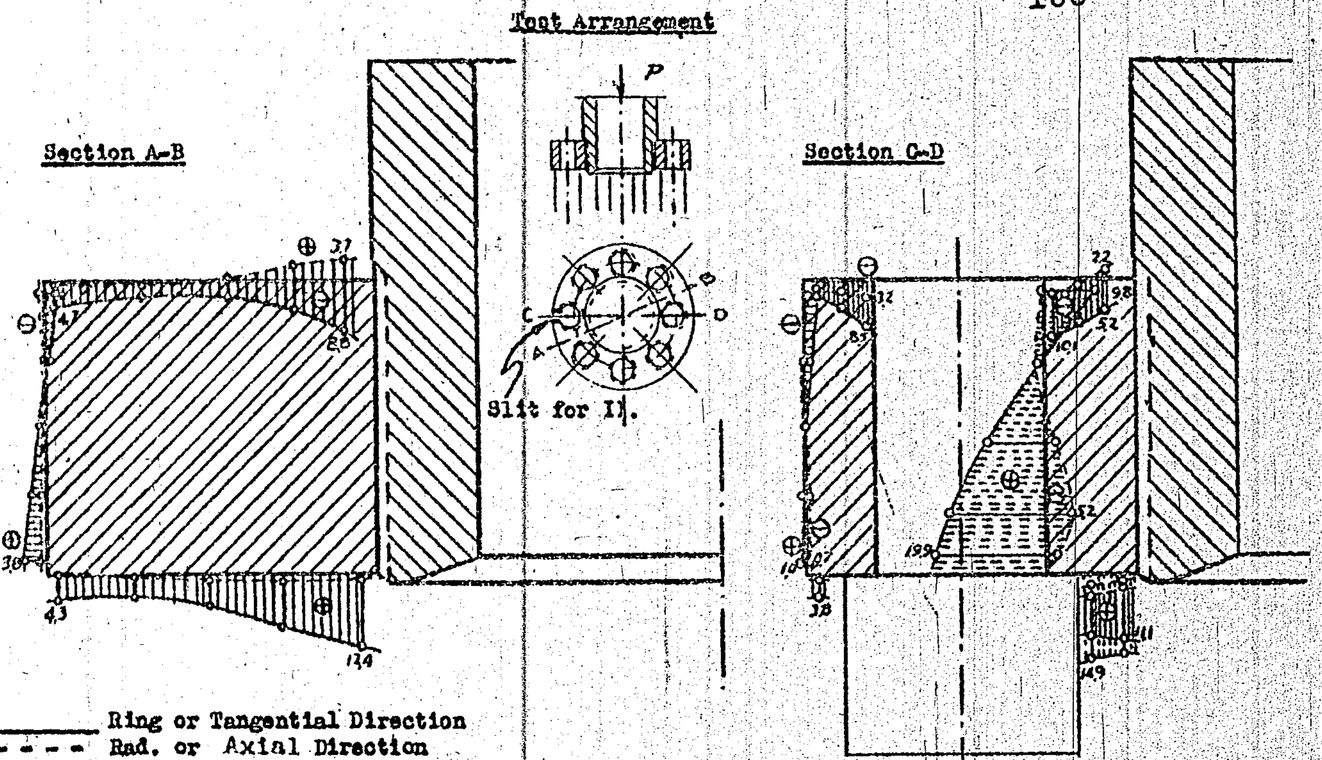
Ring or Tangential Direction
- - -Rad. or Axial Direction
P = Pi (Test Press) + 30% (add lead on bolts for tightness)

Measured Strains ε x E in kg/mm^2 between P = 0 & 80 ton.
I. ▤ on normal flange
II. ▨ with slit bolt hole

DEFORMATION MEASUREMENTS ON A 120 M.M. - 325 ATM. THREADED FLANGE.

T-228
SK 1

T-228
SK 2



──────── Ring or Tangential Direction
- - - - - - Rad. or Axial Direction
P = P1 (Test Press) - 30% (add lead on bolts for tightness).

$$S_1 = E \times \frac{1}{1-(1/m)^2}\left(\varepsilon_1 + \varepsilon_2 \frac{1}{m}\right)$$

Stresses σ_1 = E x [illegible] kg/mm^2 between P = 0 & 80 ton.

I. ──────── on normal flange.
II. - - - - - with slit bolt hole

DEFORMATION MEASUREMENTS ON A 120 M.M. - 325 ATM. THREADED FLANGE.

U. S. Bureau of Mines 197 T-229
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2-5-47

TEMPERATURES OF FLANGES AND BOLTS IN RELATION TO PRODUCT TEMPERATURE

Ludwigshafen, 9 April, 1942.

The attached diagram shows the results of a general inquiry into the temperature of flanges and bolts on high pressure lines not insulated. We propose to use the temperature curves as a basis for design of flanges and bolts for high pressure lines.

We should like to remark hereto, that these values include a certain factor of safety, inasmuch as we have considered the higher measured values. The minimum values are conditioned upon special installation conditions or very low outside temperatures.

If we, therefore, select construction materials based on these temperature ranges, we must assume that the hot flange connections are not insulated.