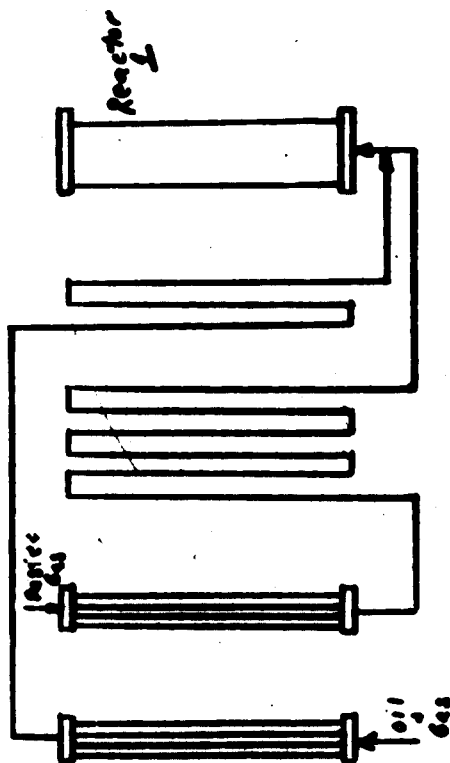


(m) The Use of Oil Feed in Cold Regenerators.

(1) Recently, a catalyst chamber using oil feed was built. In this way extra quantities of outside oil could be converted, increasing total production, as oil feed only requires half the hydrogen required for coal.

(2) At the same time, the salt deposits on the first chamber in the stalls could be removed by dilution.



Apparatus
Layout

Fig 92

FIG 13

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II. HIGH PRESSURE HYDROGENATION. (m)(Cont'd.)

(3) The oil conversion takes place with smaller heat of reaction than with coal and requires higher conversion temperatures. Since the maximum allowable temperature (21.5 M.V.) in the coal paste preheater tubes must not be exceeded (on account of salt deposition), the heating of the oil must take place in special separate tubes. Hence part of the circulating gas stream is used with coal paste as before, and part with the oil. The latter is highly superheated so that the mixture of the two final streams is 22.5 M.V.

(4) The arrangement led also to a saving of heat in the cold heat exchanger. Also the preheater tubes could be overheated without danger because no deposits occur with oil circulation. Further the deposits on the coal tubes were less, due to the lower temperatures of the exhaust gas circulated around the same. The arrangement is shown in the accompanying sketch (Fig. 13).

(5) The catalyst chamber operated fifty (50) days with a feed rate of from forty (40) to forty-five (45) cubic meters/hour and resulted in an increase in total production of one thousand (1,000) tons/month.

(6) The heat released in the cold heat exchanger amounted to five hundred thousand (500,000) kilogram-cal./hour. The resulting scale on the oil tubes in the first chamber was only two (2) to five (5) millimeters thick as opposed to forty (40) to sixty (60) millimeters in the coal paste tubes, which is harder and sticks to the walls. By increasing this oil quantity it is definitely possible to decrease the salt deposits or even eliminate them entirely. It is also important from the number of preheater tubes required, especially since the hairpin tubes are very costly.

(7) In conclusion it can be said that caviar formation can be eliminated by withdrawing part of the product stream from the first chamber and that salt deposits can be reduced by simple means, but that these steps are not of practical importance.

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II. HIGH PRESSURE HYDROGENATION. (Cont'd).

(n) Asphalt Decomposition.

(1) Asphalt is precipitated in the sump phase production of gasoline. The analysis of asphalt is very difficult since the formation of asphalt is not easily understood. It was impossible to obtain reliable results with the I. G. Ludwigshafen and Leuna methods. Therefore the following analysis was developed at our laboratory.

(2) Two (2) grams of the solid free oil is placed in a three hundred (300) cc. Erlenmeyer flask, and dissolved in ten (10) cc. pure benzol at room temperature; one hundred ninety (190) cc. of n-hexane are added and the flask shaken vigorously for about a minute. After standing one (1) hour in the cold, the contents of the flask are filtered through an extraction thimble and rinsed with n-hexane. Occasionally a thin layer of asphalt adheres to the wall of the flask and this is dissolved in benzol and added to the rest of the contents.

(3) The extraction is continued for one (1) hour in a cold extraction apparatus so that the asphalt is completely freed of the adhering oil. To prepare the asphalt for weighing the air dried thimble is extracted hot in a Soxhlet apparatus with pure benzol for one and one-half (1½) hours. After the above mentioned extraction the asphalt residue is placed in a tared flask. After evaporation of the benzol, and standing one-half (½) hour in a dessicator, it is weighed.

(4) The asphalts prepared from lignite oils are very resistant to hydrogenation. The principles of the hydrogenation process are applicable to asphalt decomposition. This decomposition is a function of the outside oil feed, the catalyst and sulfur contents, the contact time, and the operating difficulties.

(5) The outside oil was formerly used as road oil. No more than five (5) percent of the latter could be used in the diluent oil, since it would raise the asphalt content and cause difficulties in the centrifuging of the mud residue.

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II. HIGH PRESSURE HYDROGENATION. (n)(Cont'd.)

Catalyst and sulfur to the extent of five (5) percent and 1.25 percent, based on dry coal, were sufficient.

(6) The principal operating difficulties were:

- ((a)) The chamber temperature;
- ((b)) The H₂ partial pressure in the gas through-put was estimated;
- ((c)) The contact time in the reactor determined the thickening of the mud discharge since the latter carried the asphalt.

(7) These operating difficulties were interdependent as for example an increase of the temperature at a constant mud residue concentration allowed the recycle gas to be decreased, while the thickening of the mud residue was influenced by the temperature and the flow of the gases in the paste.

(8) In operation the inlet temperature was highest, principally to permit a high reaction temperature. It was held between twenty-five (25) and twenty-five and three-tenths (25.3) M.V. maximum. The mud residue concentration was also held constant, between twenty (20) and twenty-two (22) percent. It was necessary to have a positive inlet gas flow which was about twenty-eight thousand cubic meters/hour, disproportionately low, and gave an H₂ partial pressure of about four hundred fifty (450) atmospheres at the reactor inlet and three hundred (300) atmospheres at the exit. The asphalt content of the mud residue contained fourteen (14) to sixteen (16) percent and met the operating specifications.

(9) In an emergency on account of a quick shut down of the heat exchangers the recycle gas to a reactor was about fourteen thousand (14,000) cubic meters/hour. The reactor temperature was raised to the highest permissible degree of twenty-five and three-tenths (25.3) M.V. The asphalt content of the mud was sixteen (16) percent only slightly over normal. A slight H₂ pressure change can be controlled by a high conversion temperature.

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II. HIGH PRESSURE HYDROGENATION. (n)(Cont'd.)

(10) It was felt on this basis that the effect of the H_2 partial pressure was not appreciated. In short tests with our coal at Leuna at various H_2 partial pressures it was proved that the influence was very pronounced. For an increase of partial pressure of the H_2 of one hundred (100) atmospheres, the asphalt content was lowered about one-third (1/3) of the previous value.

(11) This observation resulted in the introduction of fresh H_2 in the hot heat exchanger and an improvement of several percent in the asphalt plant.

(o) The Introduction of Fresh H_2 in the Hot Separator.

(1) In connection with the difficulty of decomposing the asphalt, the sludge tended to coke in the separator. The tendency was influenced by increased solids concentration. In operation the upper limit was twenty (20) to twenty-two (22) percent.

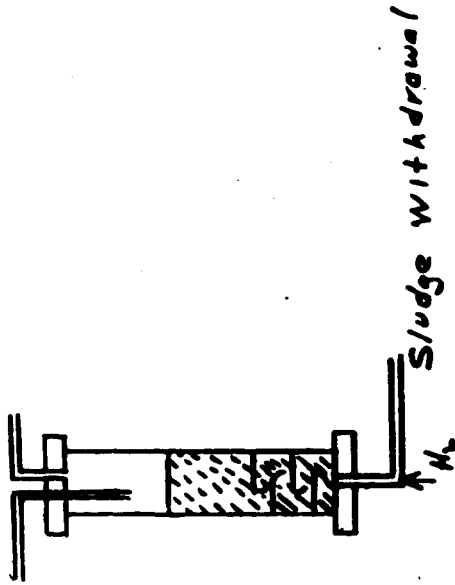
(2) A precaution against coking was used. Asphalt-free oil was fed to the sludge and recycle gas added to the outlet cone in the separator. The oil injection was reduced while the extremely effective gas introduction was maintained. Later through the substitution of fresh gas for recycle, the operation was improved.

(3) The fresh gas addition, apart from the more effective prevention of coking of the sludge, lead to the following improvements. The hydrocarbons dissolved in the sludge would be removed from the recycle gas stream and in the normal operation added to the sump chamber products.

(4) Propane and butane were produced mostly as power gas and the higher hydrocarbons as middle oil fraction. The residue gas had a H_2 content of over ninety (90) percent as against sixty (60) percent previously and it was as suitable as new H_2 for hydrogenation.

(5) A part of the heat removed with the sludge was carried in the circulating gas, and this was used in the heat exchanger.

Fig. 14
Countercurrent
Hot Separator



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II. HIGH PRESSURE HYDROGENATION. (o)(Cont'd.)

(6) The addition of the sludge gases to the fresh gas disturbed the hydrocarbon content of the resulting sludge-desanding gases. This liability was one of the reasons for the rebuilding of the de-sanding apparatus in the so called reactor 1 - reactor 2 - de-sanding. With its use, desanding product did not accumulate and therefore no de-sanding gas was lost any longer.

(7) The high H₂ partial pressure of the fresh gases caused a hydrogenation of the sludge oils and likewise they were cooled by the inlet gas. The hydrogenation caused an increased oil yield in the chambers. The hydrogenation had to be greatly intensified to maintain the temperature in the hot separator. An apparatus was constructed for this to contact the liquid and gas counter-currently in a small space. The installation of the small hot separator increase the reaction space (Fig. 14).

(8) It is used for heat exchange purposes and contains several indented baffle plates which have a gas space on the lower side. This produces a good gas distribution. Gas and liquid are thoroughly contacted in their counter-current flow between the plates. By keeping the velocity of the liquid phase lower than the gas phase a back flow of the cooled liquid is prevented. Accordingly a good heat exchange is obtained between the sludge and fresh gas. The temperature is controlled in the upper part of the separator by cold gas inlet.

(9) The total requirements of a chamber can be met by a fresh gas flow of about fifteen thousand (15,000) cubic meters/hour. The discharged sludge is cooled about one hundred fifty (150) to two hundred (200) degrees centigrade. The heat exchanger and cooler may be omitted in the sludge discharge.

(10) A separator of this type was used several days before operation of the plant ceased. In this short time, only the heat exchange operation could be investigated and was found to be exceptionally good.

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II. HIGH PRESSURE HYDROGENATION. (o)(Cont'd.)

(11) The hydrogenation was tested in a similar but packed separator, but the heat exchange was not complete as only four thousand (4,000) cubic meters/hour fresh gas could be used. The asphalt content of the sludge oil was reduced from sixteen (16) to twelve (12) percent. It is possible that the asphalt decomposition may still be improved by the use of higher H₂ flows past the baffle plates.

(p) Erosion in the Preheater Tubes.

At the beginning of 1943 the inside surface of the preheater tubes was noticed to have cuts six (6) millimeters deep. In previous operations no erosion had been observed. Meanwhile the charges to the chambers had been increased, and the erosion was related to the increased throughputs. It followed that it conformed approximately to the MV³ value of the mass and velocity.

(q) MV² in the Preheater at Different Feed and Gas Rates.

(at 420°C. preheater temperature, 650 atm. pressure, 0.380 gas density and 1.000/420°C. sp. grav. coal paste)

Gas m ³ /hr	Coal Paste m ³ /hr	Velocity m/sec	Mass Coal Paste + Inlet Gas	MV ²
27,000	35,000*	6.4	12.6 (units?)	516
27,000	40,000	6.6	14.0	610
27,000	45,000	6.8	15.4	712
13,000	40,000	4.1	12.5	210
13,000	45,000	4.3	13.9	257
13,000	50,000	4.5	15.3	310
10,000	40,000	3.6	12.1	157
10,000	45,000	3.8	13.5	195
10,000	50,000	4.0	14.9	239

* These values obviously should be 35,000, etc.

(1) The table shows that the inlet gas flows must be reduced when the coal paste throughput is raised. Therefore

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II. HIGH PRESSURE HYDROGENATION. (q)(Cont'd.)

the paste throughput was held constant, and of the twenty-seven thousand (27,000) cubic meters/hour outlet gas, twelve thousand (12,000) cubic meters were added directly to the hair pin bends and to reactor. This method of operation stopped the erosion.

(r) The Heat Exchangers.

(1) The operation of the heat exchangers in the surp phase was unsatisfactory when operated with only coal paste. The chief reason was the deposition of heavy solid matter out of the coal paste onto the walls of the tube bundle. It resulted in plugging of the inner passages of the tubes. Analyses showed that the deposits were chiefly catalyst, while the inside of the tubes were corroded by H₂S. Part of it was traced to the sludge discharge.

(2) Analyses of the deposits of a heat exchanger compared with the analyses of the catalyst and ash analyses of coal paste and sludge.

Non-combustible Analysis of non-combustibles

	%	CaO	Fe	S	Al ₂ O ₃
Deposit outside of tubes	78.5	12.7	31.5	15.4	8.8
Deposit inside of tubes	91.5	7.3	43.9	20.6	6.3
Coal paste + Solids	14.	23.9	23.5	9.5	10.7
Sludge + Solids	84.5	23.9	23.5	9.5	10.7
Catalyst	100.	2.2	38.2	21.8*	18.6

* Calculated

(3) The original remedy of operating both exchangers with paste-gas mixtures was stopped. Only the hot exchanger is run with paste-gas mixture, and the cold one is operated with gas.

(4) Additional studies were made with smaller tube bundles in an attempt to decrease the solid deposit through increase in the fluid velocity. Instead of the usual one

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II. HIGH PRESSURE HYDROGENATION. (r)(Cont'd.)

hundred ninety-nine (199) tube bundle, ones with one hundred fifty (150) and one hundred eight (108) tubes were made and so the velocity of the paste-gas mixtures were raised from 0.4 meters/ second to 0.6 and 0.8 meters/second. A further study was made of a modification of the upward flow of paste, and gas in a down-flow, process.

(5) The following table shows the operation times of the bundles with paste-gas mixtures with various arrangements.

Average Operating Periods of Heat Exchanger Bundles

	Total days	Days when K value was over 100
1. Charging both exchangers with paste-gas mixtures in down flow	55	41
2. Charging only the hot exchanger with paste-gas mixture		
199 tube bundles up flow	95	70
150 " " " "	95	67
108 " " " "		61
199 " " down flow	104	81

(6) The distribution in the gas-paste exchanger caused an increase in efficiency, while the shortening of the bundles caused a decrease. Nevertheless even by this method of operation special results may be expected. This reverse of fluid flow led eventually to a greater improvement, and since the results were not satisfactory, the answer was sought through change of the exchanger construction.

(7) An Exchanger with Paste Down-Flow and Gas Up-Flow.

((a)) This method of operation differed from the previous paste-gas down-flow, since in gas up-flow the exchanger is filled with liquid while in gas.

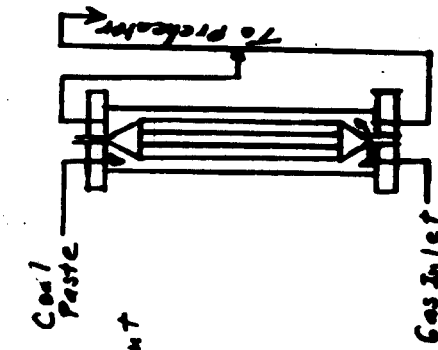


FIG. 15
Heat Exchanger
With Counter-Current
Flow of Paste and
Gas

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II. HIGH PRESSURE HYDROGENATION. (r)(Cont'd).

down-flow it is empty. In the gas down-flow method heavy solids in the liquid settled out.

((b)) In the exchanger full of liquid a drying and agitation of the paste by the gases occurred. The pressure of H_2 is indispensable from a chemical standpoint to prevent flow stoppages (due to deposits). During the operation it was noticed that the exchanger must be kept full of paste and that the paste must not be allowed to overflow the top or the gas to discharge from the bottom. The arrangement is shown in Fig. 15.

((c)) The joining of the gas and paste outlets, half way up the column prevented the paste from being carried out in the gas streams, and the liquid-gas interface was kept constant.

((d)) A direct injection of the gas into the paste outlet is only done with large gas flows.

((e)) A heat exchanger of this construction was in operation twelve (12) days before the closing of the plant. As opposed to this, the previous exchanger had to be cleaned after twelve (12) days operation to restore the K value. The new construction did not require cleaning. It operated well and used two million eight hundred thousand (2,800,000) kilograms cal./hour less. For this the nine (9) meters long hat separator should find application, since by remodeling the last reactor for fresh gas injection, the counter-current separator would be freed. Heavy oil is added to the regular gas stream at the entrance to the exchanger.

(8) The Cleaning of Plugged Exchangers.

((a)) This is costly and time consuming. Previously it was necessary to build the exchangers separately so that by taking off the heads the tube bundle could be withdrawn.

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II. HIGH PRESSURE HYDROGENATION. (r)(Cont'd.)

((b)) The repair methods of other plants were not suitable for Wesseling. It is obvious that the cleaning of plugged exchangers with a suitable flushing oil would simplify matters. This method could be used to good advantage by all hydrogenation plants. It was desired to inject CO₂ at high velocity through the exchanger. At the same time high pressure steam would be passed through the tubes. (Fig. 16).

((c)) For a dissolving medium, diluent oil is desirable since it has been shown by laboratory tests to be a good cleaning agent for the deposits on the tube bundles. The flushing would be continued for several days with repeated oil changes.

((d)) The cleaned exchanger could not be tested on account of the plant shut down. The solid matter lost was not great as in the previous method. The cleaning left the exchanger with a pressure drop no greater than in a new one, and the K value was increased to a serviceable figure.

((e)) If the tubes on the inside are plugged too tight, and a high pressure steam or the previously mentioned flushing does not produce the desired results then a mechanical cleaning is necessary. The tube bundles are removed, new ones installed, and the old ones cleaned. This saves production time.

((f)) The flushing with oil and CO₂ played a large part in reducing costs of exchanger maintenance.

(s) Machines.

In spite of the war and the supply difficulties of all of the stuffing box materials, all machines operated trouble free so that no production loss resulted on this account.

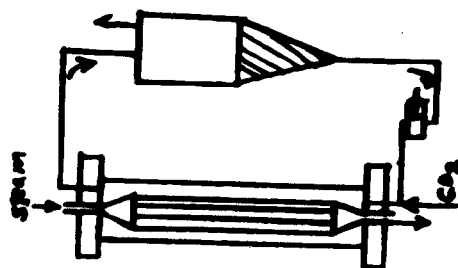


FIG. 16
Heat Exchanger
Flushing with Oil
and CO₂ Injection

Fig 17

Bearing
Arrangement of the
700 Atm
Circulating
Pumps

