

## II. HIGH PRESSURE HYDROGENATION.

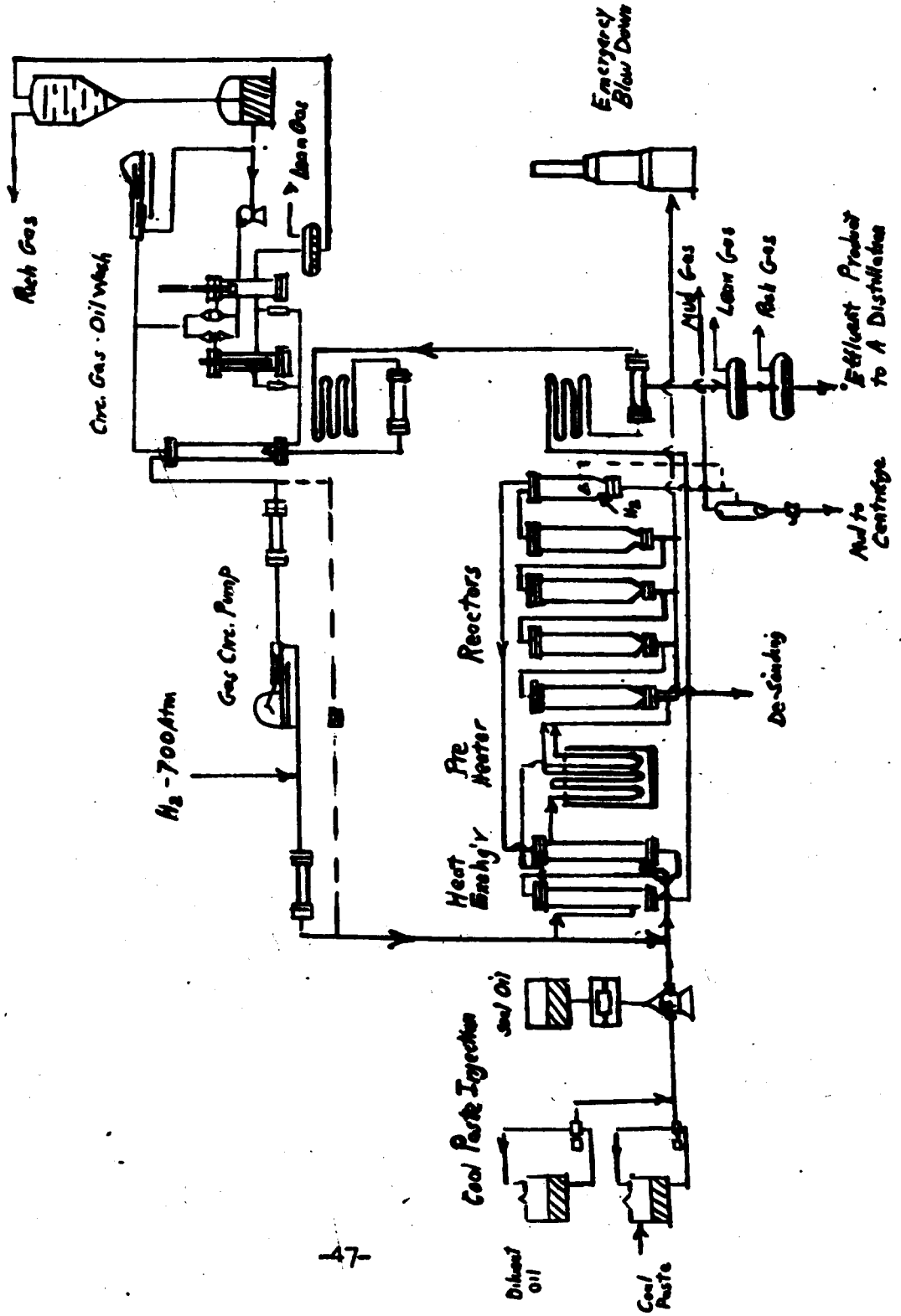
(a) The unit consists of four (4) stalls, five (5) gas circulating pumps, sixteen (16) paste presses, and pumps for seal oil and water, as shown on the attached diagram (Fig. 11). Also an oil, recycle gas washing unit with preliminary circulating gas cooler, intermediate expansion tanks for both the effluent and wash oil.

(b) Each stall has four (4) chambers and includes two (2) heat exchangers sixhundred millimeters diameter, a single burner preheater having eighteen (18) to twenty (20) hairpin tubes ninety (90) to one hundred (100) millimeters diameter, and two (2) circulating gas blowers. Two of the reactors are eighteen (18) meters long and two are fifteen (15) meters long, all one thousand (1,000) millimeters in diameter. There is also in each stall an air and water cooler for the muds, and after-coolers for the effluent product. The first reactor chamber has a de-sanding device.

(c) Due to packing trouble, the gas circulating pumps were changed from plunger to piston type, piston diameter equal to two hundred (200) millimeters. The circulating pumps handle seventy-two thousand (72,000) cubic meters/hour at a differential pressure of eighty (80) atmospheres.

(d) The coal paste is injected by sixteen hydraulically operated presses, each handling ten (10) cubic meters/hour. Lately, two more twenty (20) cubic meters/hour presses were added. The circulating gas is washed in three towers each twelve (12) meters long, one thousand (1,000) millimeters in diameter, and attached are three (3) expansion machines handling sixty-five

OG. 11  
High Pressure Hydrogenation  
Sump Phase



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

(65) cubic meters/hour, four (4) feed pumps of ten (10) cubic meters/hour capacity each and one wash oil degasifier pump operating at atmospheric pressure.

(e) The intermediate expansion units for effluent and wash oil are designed for fifty (50) atmospheres operating pressure.

(f) In the sump phase lignite outside oil and H<sub>2</sub> are converted to middle oil as follows:

CRACKING AND HYDROGEN ADDITION IN THE PROCESSING OF COAL  
IN THE SUMP PHASE

	<u>LIGNITE</u>	<u>MIDDLE OIL</u>
avg. mol. wt.	over 1000	220
Carbon atoms	over 100	14
H <sub>2</sub> content	2 %	10 %

(f) Description of the Process.

(1) The coal paste from the mill unit is first screened in a vibrating screen. The oversized reject normally runs 0.3 kilograms per ton of paste. Most of the rejects can be mixed with screenings of dry coal along with heavy grinding substances in proportion of 2.0 kilograms /ton paste. As it contains forty (40) percent oil it is easily marketed as fuel. The paste is then taken to the high pressure paste injection pumps by piston type pumps. The former delivers the paste to the reactors. The suction lines of the paste presses are connected to the diluent oil circulating system. A quick change over from paste to diluent oil is possible by merely manipulating two (2) valves. This is done at every starting and shutting down of the unit because the evaporation of the diluent oil can quickly reduce the chamber temperature. For protection, the glands of the paste presses are sealed with this oil.

(2) The paste and gas, rich in H<sub>2</sub>, pass through heat exchangers to a preheater and then into the catalyst chambers. The circulating gas flows through a cooler, and then

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

is split into equal streams. One-half joins the paste entering the hot heat exchanger and there through the preheater to the first chamber, while the second half goes through the other preheater section directly to the first chamber. The preheater uses gas fuel whose smoke is removed by blowers. The temperature of the circulating gas must remain below the maximum allowable creep temperature of the heater tubes. The temperature of the paste gas mixture is held as low as possible, not only to save heating gas, but because temperatures over three hundred seventeen (317) degrees centigrade (21.5 M.V.) cause salt deposits.

(3) The cool paste is decomposed in the catalyst chamber at four hundred seventy-eight (478) degrees centigrade (25M.V.). This temperature is controlled by injecting cold circulating gas.

(4) On the underside of the first chamber is a de-sanding device, through which one thousand (1,000) to one thousand five hundred (1,500) liters/hour of material is removed. This greatly reduces "caviar" formation in the form of spherical lumps of  $\text{CaCO}_3$ . The conversion products are carried off in vapor phase in the circulating gas stream. The ash content tends to mix with the heavy boiling oil and accounts for the discharge mud leaving the last chamber. The solid content of the mud runs around twenty (20) to twenty-two (22) percent and sets the temperature of the chamber. The solid content of the mud tends to coke up in the heat exchangers due to lack of hydrogen. The coking can hence be eliminated by injecting fresh  $\text{H}_2$ . This also helps to strip the dissolved gaseous hydrocarbons from the mud.

(5) The mud is cooled to one hundred fifty (150) degrees centigrade and expanded to atmospheric pressure by special valves, having seats and gloves of tungsten carbide. It is then pumped over to the mud disposal plant. The gas released from the mud contains over ninety (90) percent  $\text{H}_2$  which can be used over again as fresh hydrogen.

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

The product stream from the catalyst chambers passes through heat exchangers and coolers. The liquid cut is condensed and enters the coal liquid stripper. The temperature in the latter must be kept above one hundred twenty (120) degrees centigrade in order to prevent foaming. The Bottoms product from this is next expanded and distilled. The expansion occurs in two stages and the released gas separated into a rich and a poor hydrocarbon fraction.

(7) The non-condensable gases are given an oil wash under high pressure and the subsequent hydrogen remaining in the gas is used over again in the re-cycle stream along with fresh hydrogen make-up.

(8) The oil wash unit consists of a high pressure wash tower, a wash oil stripper, and an injection pump for the tower. The wash oil used is the product from the gas phase gasoline reactor. The washing is regulated to give a gas of gravity of 0.35 which corresponds to a hydrogen content of seventy (70) to seventy-five (75) percent. The wash oil regeneration is done by expansion in two stages.

(9) The circulating gas temperature is always kept above thirty (30) degrees centigrade to prevent the deposition of hydrates and ammonium bicarbonat.

(g) Operating Data and Product Analyses.

Paste feed	40 cu.meters/hr. (in chamber 31 cu. meters)
Catalyst added	5 % red earth ( $Fe_2O_3$ ) based on dry coal.
Sulfur added	1.25% red earth ( $Fe_2O_3$ ) based on dry coal.

(h) Paste Analyses.

Solids	41.0 %
Pure Carbon	35.6 %
Ash	13.3 %
Iron	3.0 %

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

Sulfur	1.6 %
Sp.Gr. @ 110°C	1.175
H <sub>2</sub> O	1.90
Screen oversize (above 3 mm. mesh)	10.6 %
Gas feed	28,000 cu.meters/hr.
(Paste gas)	13,000 cu.meters/hr.
(Direct to chamber)	15,000 cu.meters/hr.
Cold Gas (quench)	12,000 cu.meters/hr.
H <sub>2</sub> content (Stall entrance)	73.0 %
Pressure	650 atm.

(i) Temperatures.

(1) Chamber 1	22.5 - 25.0 MV
Chamber 2	25.0
Chamber 3	25.0
Chamber 4	25.0
Coal converted	99.6 %
Middle oil produced	0.275 tons/cu.m. reaction space.
Effluent product based on coal paste	50.0 %
Mud product based on coal Paste	33.3 %
Middle oil - 360°C end point - in effluent product	39.0 %
Middle oil - 350°C end point - in mud	11.0 %
Solids in mud	20.0 %
Asphalts in mud oil	16.0 %

(2) Important difficulties in the sump phase prevented continuous perfect operation. These were:

- (a) Difficulties with water separation, causing foaming in the product streams.
- (b) CaCO<sub>3</sub> deposits causing caviar and salt crust formation.
- (c) Injurious asphalt formation and coking in the product cooler.

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II. HIGH PRESSURE HYDROGENATION. (1)(Cont'd).

(d) Preheater tube erosion from sudden product stripping.

(j) The Effluent.

(1) The coal stall effluent when processing pure Rhine lignite has a high specific gravity. It runs from 1.00 to 1.03 at twenty (20) degrees centigrade. This makes ordinary separation of the water of reaction (which must occur before distillation) impossible. Instead, ten (10) to fifteen (15) percent of a special light oil must be added which is the product from the gasoline chamber of the subsequent gas phase operation. The resulting specific gravity of 0.97 at fifty (50) degrees centigrade allows for complete and easy separation.

(2) The effluent also tends to foam, causing trouble in the circulating gas pump and wash system. The foaming can be eliminated by maintaining an effluent temperature of one hundred twenty (120) degrees centigrade.

(k) Caviar and Salt Deposits.

(1) In hydrogenation, the term "caviar" refers to the formation of inorganic products of coal decomposition in the form of small spheres. At Wesseling, this caviar formation took on a size not seen before in other plants. Frequently all four (4) catalyst chambers in a stall would be filled up after ten (10) days operation. At the same time the caviar was forming, salt encrustation of baffles and chamber interiors was taking place. Caviar and salt deposits are chemically alike and contain almost the same amount of  $\text{CaCO}_3$ .

	Residue after		Ash Analyses						
	roasting		CaO	CO <sub>2</sub>	MgO	S	Fe	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
Caviar	58.4%	46.3	31.8	2.9	1.4	1.8	3.1	0.1	7.1
Salt Crust	59.4%	47.0	26.0	4.5	1.5	4.0	1.7	0.5	5.6

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

(2) Caviar formation results in poor operation as it quickly reduces the available catalyst chamber volume and leads to all kinds of mechanical difficulties. The loose caviar also gets baked into the material being processed, and finally results in a solid mass, requiring a complete overhaul and cleaning of the unit. Such cleaning is difficult and requires time and materials.

(3) The exact cause of caviar formation has often been discussed. Means used at Wesseling for preventing its formation indicate its origin, namely that it is definitely related to the disintegration phase of coal, which occurs in a zone at the lower part of the first chamber. Hence its growth can be prevented if the crystallization nuclei and the small particles themselves are removed. This is done in a de-sanding apparatus through which part of the product stream from the first chamber is passed, under a long soaking time which breaks down the crystal structure of the caviar. The process can be seen on the attached diagram (Fig. 12).

(4) The method has been used at Leuna for some years. The exact Leuna arrangement could not be used here and had to be changed. In Leuna, one hundred (100) to two hundred (200) liters/hour of product were removed, while at Wesseling one thousand (1,000) to two thousand (2,000) liters/hour had to be withdrawn. Such quantities could not be withdrawn in the Leuna system without causing very large gas losses.

(5) The reason for this is as follows:

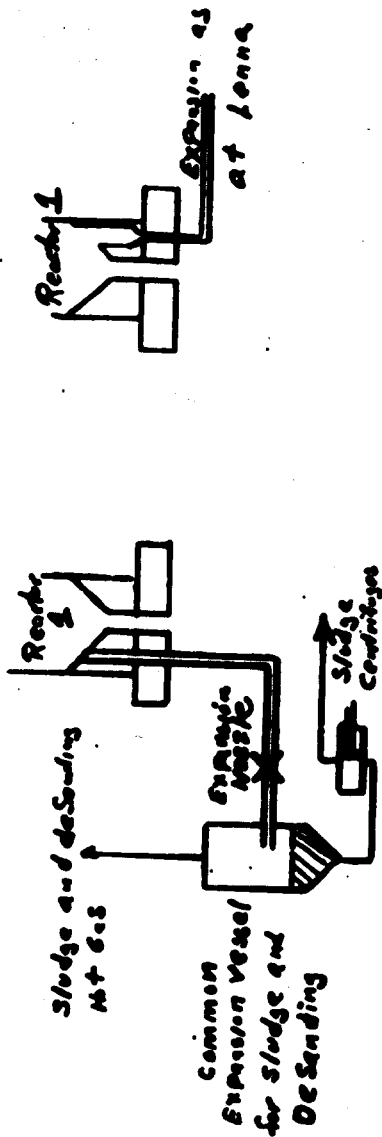
The expansion of the de-sanding product takes place batchwise in the horizontal part of the piping through orifices. To do this, the orifice is fully opened for one (1) to two (2) seconds allowing the pipe to become completely empty, while at the same time material is coming into the pipe from the catalyst chamber. The material contains a large quantity of gas, because its high discharge velocity does not allow for a separation of gas and liquids. In the time interval until the next blow-down, liquid fills the gas space resulting in the wrong proportions of gas to liquid.



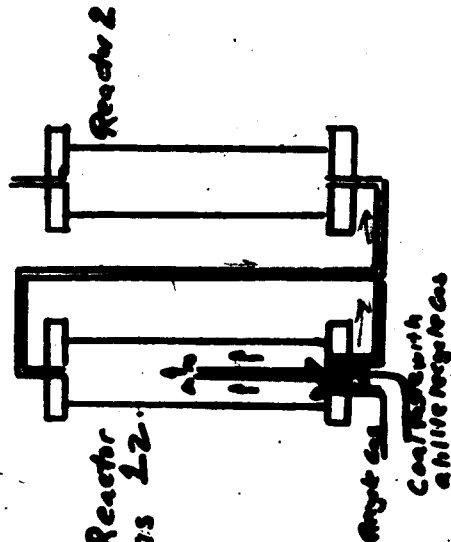
FIG. 12

Desanding Process  
at I.G. Leuna

Wesseling



Principle of Reactor  
The Best Desanding Apparatus 12.



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

Hence gas and liquid expand through the orifice into the next catalyst chamber. In Leuna, this difficulty did not occur because the chambers are raised on supports and also because the vertical pipe is proportionately long. To solve the problem at Wesseling, a six (6) liter bottle was attached to the forty (40) millimeter diameter blow down line under the funnel of the first catalyst chamber.

(6) Because of the excessive erosion of the expansion orifices, and also the difficulty in replacing the parts due to material shortage, a de-sander without orifices was developed. A further reason for this new design was the large product and gas loss formerly entailed. In the new design, the de-sanding product was no longer expanded but put into the second catalyst chamber. The diameter and length of the connecting pipe was fixed to maintain a constant pressure drop of one (1) atmosphere between the two (2) chambers. The flow velocity was not allowed to drop below 1.5 meters/second hence preventing the settling out of heavy products. Means were taken to remove the causes of caviar formation in the second chamber, by putting a vertical internal coal paste feed pipe in the first chamber. After a fifty (50) day operating period, no caviar was found in the second chamber.

(7) Salt deposits like caviar also cause trouble despite the results of Leuna and Ludwigshaven for avoiding the same. In the experimental pilot plants, heavy deposits were found on all hot parts of the unit, especially in the catalyst chambers. Attempts were made to eliminate this by chemical means adding  $H_2SO_4$  or S, with no success. It was definitely proven however, that the formation is a function of temperature. This starts at nineteen (19) M.V. and increases with higher temperatures. At Wesseling the limit was somewhat higher, 21.5 M.V. The heaviest deposits occur in the caviar forming zone which is the lower section of the first chamber. Deposits as thick as fifty (50) millimeters were found on the chamber sides and on both the hot and cold hydrogen tubes. The deposit on the piping between chambers one and two was ten (10) millimeters thick, and in subsequent piping only slightly less so. The effect on the

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

preheater tubes is serious as it cuts down the heat transfer and results in overheating the tubes. At Wesseling, the relatively high formation temperature of 21.5 M.V. makes the elimination of the deposits easy. The relatively high partial pressure of hydrogen at seven hundred (700) atmospheres in the first chamber results in a high heat of reaction so that the preheater outlet can be held below twenty-one (21) M.V.

(8) The salt deposits in the first chamber were really serious from a war viewpoint because of the time delays needed to remove them and the freeing of the clogged de-sander nozzles.

(1) Influence of Diluent Oil on CaCO<sub>3</sub> Deposits.

(1) Since salt deposits tend to increase in cold, non-insulated pipes rather than in hotter insulated ones, it is fairly safe to assume that this again is a crystallization of CaCO<sub>3</sub>, and led to attempts to remove it by injecting cold diluent oil rather than cold gas. This produced a delay of the initial formation from three (3) or four (4) days to three (3) or four (4) weeks and resulted in doubling the operating period. The nature of the material removed at the end of this time was not different from the previous operation.

(2) The oil injection was finally given up as its results were not good in that it overloaded the chamber and did not remove the caviar from the first chamber.