

III. METHANE CRACKING UNIT.

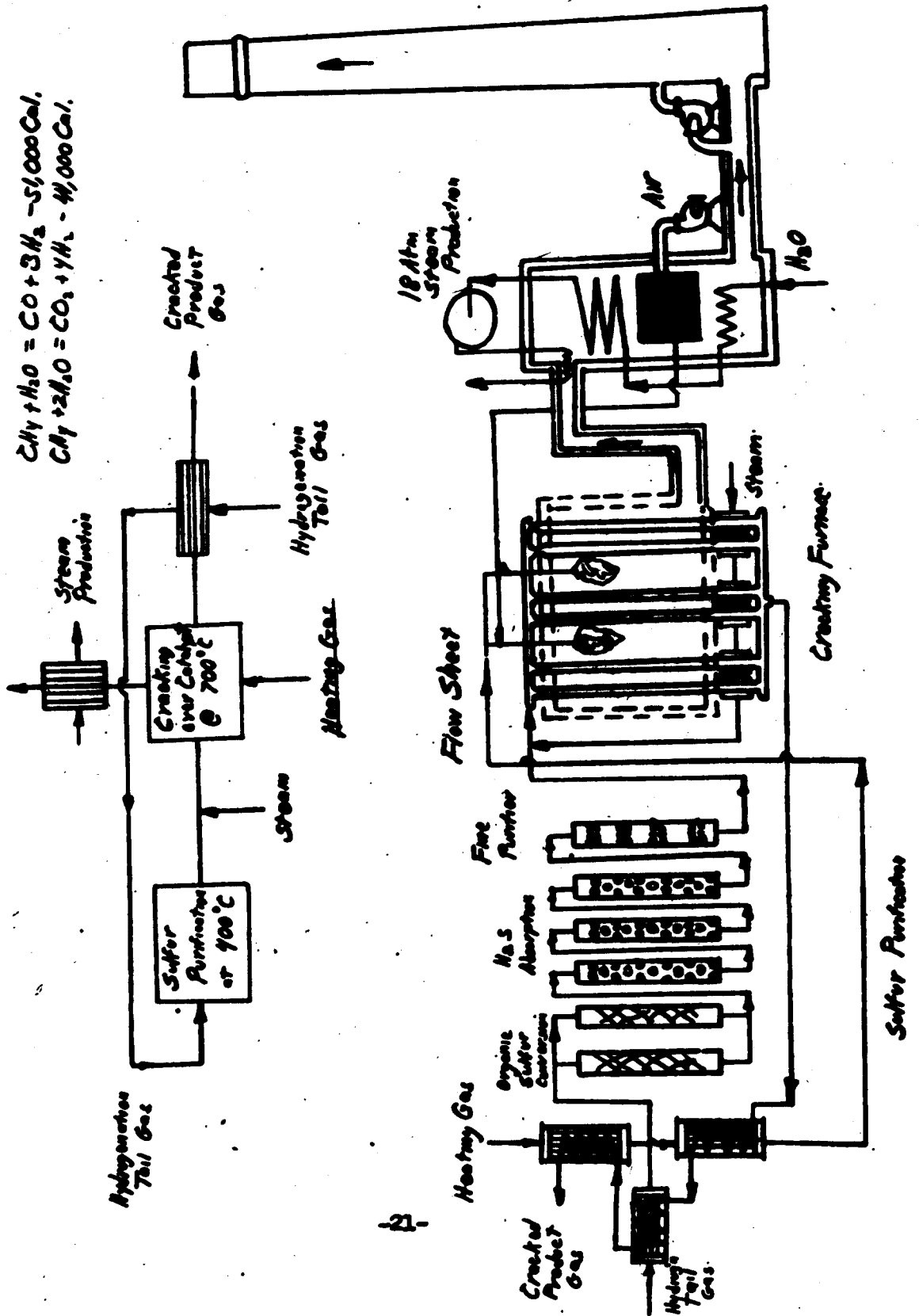
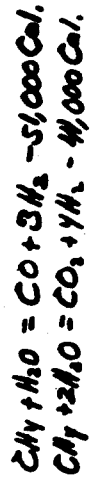
(a) This unit has four furnaces, each with sixty-six (66) catalyst tubes. In this unit the tail gas from the hydrogenation process is cracked in the presence of steam to CO_2 , CO , and H_2 as follows:



(b) The process at Wesseling is one using catalysts at six hundred (600) to seven hundred (700) degrees centigrade, as opposed to the other well known thermal cracking process operating at one thousand (1,000) degrees centigrade. The former was developed by I. G. at Ludwigshaven. The Wesseling process is shown on the attached flow diagram (Fig. 5).

(c) The catalyst used is of a nickel base and therefore sensitive to sulfur poisoning. Hence the feed gas must be very free from sulfur.

FIG. 5
Hydrogenation Tail Gas Cracking



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III. METHANE CRACKING UNIT. (Cont'd.)

(d) The reaction is endothermic and therefore requires heat other than that obtained by heat exchange. Hence the process requires a fairly complete sulfur removal unit and large heat exchangers as well as the furnace. The gas is passed first through three exchangers heated against the finished product at about four hundred twenty (420) degrees centigrade. It then enters a catalyst chamber where the organic sulfur is converted to H_2S over an Fe_2O_3 catalyst. Next, it enters a chamber containing ZnO which removes the H_2S , still at the same temperature of four hundred twenty (420) degrees centigrade. Finally it enters a "fine sulfur" removal chamber having alternate beds of Fe_2O_3 and ZnO .

(e) Steam amounting to 1.2 kilograms/cubic meter of feed is injected into the gas stream, of which 0.5 kilograms is for conversion and 0.7 kilograms maintains equilibrium. The gas now enters the cracking catalyst chamber where a temperature of six hundred fifty (650) to seven hundred (700) degrees centigrade is maintained by external heating of the catalyst tubes. The exhaust heat from the burners is used to produce steam and to preheat the combustion air.

(f) The final cracked product has a CH_4 content of 1 - 2 percent. It leaves the unit in giving up its sensible heat to the incoming gases through the exchangers.

(g) In order to insure the complete conversion of the methane, and to maintain the proper cracking catalyst life, the sulfur content must be below five (5) milligrams/cubic meter. The tail gas normally contains fifty (50) to one hundred (100) milligrams/cubic meter of H_2S and fifty (50) milligrams/cubic meter of organic sulfur. The Bamag unit, using first Fe_2O_3 for the organic sulfur, and then ZnO for the H_2S is insufficient in scope, as it only reduces the sulfur content to ten (10) to twenty (20) milligrams/cubic meter.

(h) After many experiments, the present "fine sulfur" removal system was devised using spent Nickel catalyst from the cracking chamber at four hundred (400) degrees centigrade. This reduces the final sulfur content to the operating requirements.

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III. METHANE CRACKING UNIT. (Cont'd.)

(i) The waste heat boiler was originally fed with water from the Permutit water purifier. Due to scale formation on the tubes, the water source was changed to condensate from the distilling unit. This water had to be filtered, as well as given a further treatment by injecting NaOH to neutralize the free oxygen and CO₂ therein.

(j) Through the above improvements, as well as adding an economizer to the unit, it was possible to equal the quantity of 3.5 atmosphere steam with an equal quantity of eighteen (18) atmosphere steam.

(k) Another cause of operating trouble on the cracking unit was the dust and oil content in the heating gas. As already mentioned in describing that product, its dust content was ten (10) grams/cubic meter and its oil content one hundred fifty (150) grams/cubic meter. This led to fouling of the feed gas preheater tubes, requiring quarterly cleaning, lasting one week with a corresponding loss in production.

(l) The cost of producing water gas and cracked gas are almost the same. The water gas costs 2.82 Pfg/cubic meter and the cracked gas 2.60 Pfg/cubic meter when the hydrogenation tail gas has a heating value of 0.45 Pfg/1000 W.E.

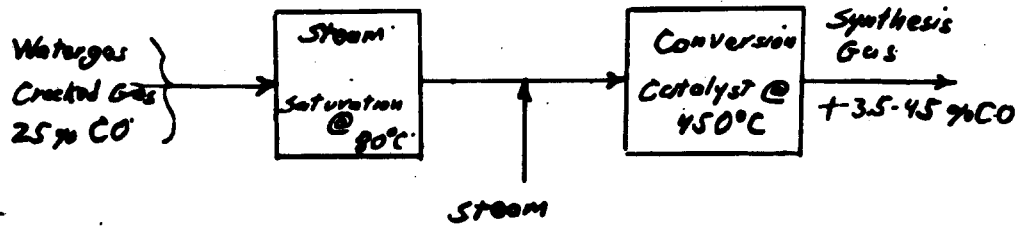
	<u>Water Gas</u>	<u>Cracked Gas</u>
Raw material and energy	16.15 R.M./1000cu.m.	21.74 R.M./1000cu.m.
Credit as by-product	H (2.27)	- (2.23)
Operating cost	3.33	1.66
Fixed charges	7.64	3.75
Other charges	3.11	1.07
	<u>28.16 R.M./1000cu.m.</u>	<u>25.99 R.M./1000cu.m.</u>

OPERATING RESULTS

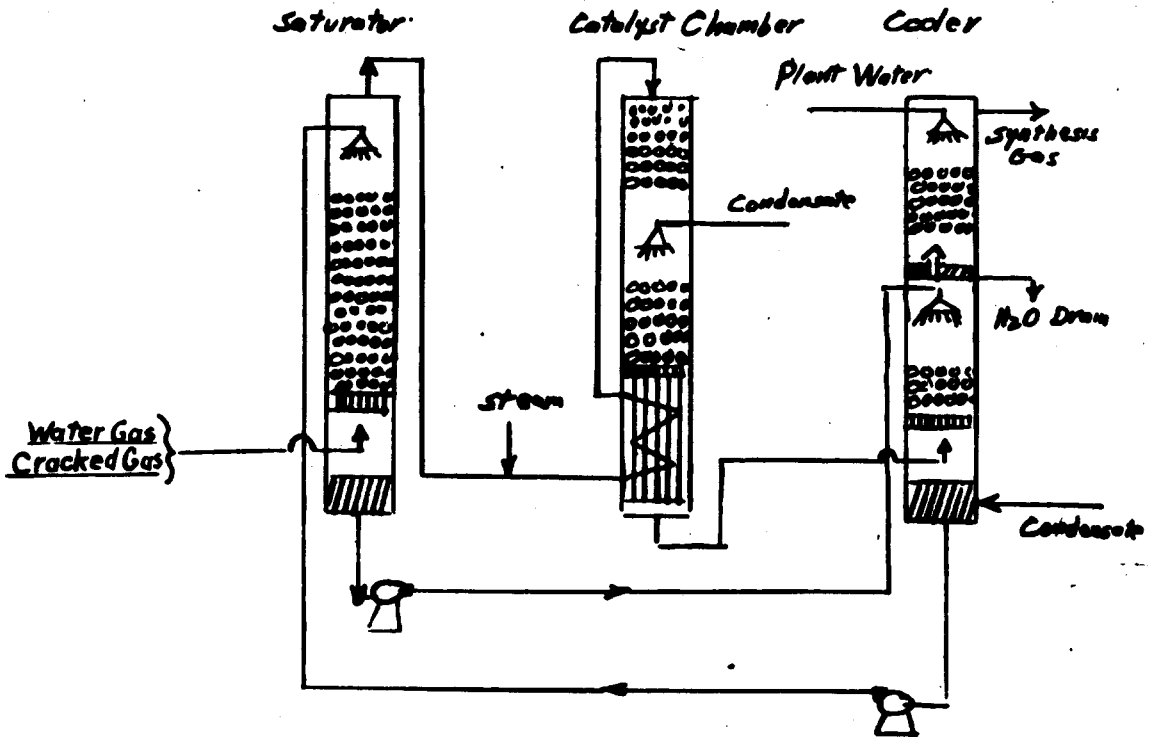
	<u>1943</u>	<u>1944</u>
Cracked gas produced	33,600 cu.meter/hr	40,000 cu.meter/hr

FIG. 6
Water Gas Conversion.

Principal



Flow Sheet



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III. METHANE CRACKING UNIT. (1) (Cont'd.)

UNIT FIGURES

	<u>1943</u>	<u>1944</u>
Cracked gas/tail gas	2,717	2,400
Heating gas/cracked gas	902 W.E./cu.m.	850 W.E./cu.m.
3.5 Atm. steam req'd/cracked gas	0.554 Kg/cu.m.	0.550 Kg/cu.m.
18 Atm. steam req'd/cracked gas	0.320 Kg/cu.m.	0.450 Kg/cu.m.
CH ₄ in cracked gas	2.7 %	1.5 %

IV. WATER GAS CONVERSION UNIT.

(a) This unit consists of fourteen (14) catalyst chambers for each seven thousand (7,000) cubic meters of gas processed and three (3) towers for saturating the incoming and cooling the outgoing gas, as shown in the diagram (Fig. 6).

(b) The CO from the water gas and cracked methane is converted to hydrogen in the presence of steam as follows:



(c) The reaction occurs at four hundred fifty (450) degrees centigrade over an iron catalyst in the presence of steam. It is strongly exothermic and hence requires no heat.

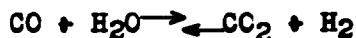
(d) The steam is either used to saturate the incoming gas or enters the reactor directly. At the same time, a small quantity of condensate is injected over the catalyst to regulate its temperature.

(e) The saturation step takes place in the saturator tower where hot water enters and is sprinkled through the gas steam. The water is heated by the outgoing gas and is circulated between the saturator and the cooler. The highest temperature possible is obtained in this water and usually reaches eighty (80) degrees centigrade.

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IV. WATER GAS CONVERSION UNIT. (Cont'd.)

(f) The gas is saturated as much as possible with water, but a limit is reached due to resistance through the catalyst chamber. In order to save steam, a lower catalyst temperature is used since the



equilibrium calls for a definite water quantity. The temperature used at Wesseling is four hundred twenty (420) degrees centigrade.

(g) The capacity of the unit was thirty (30) percent over the guarantee. Further increase was impossible due to the limitation of the water gas blower outlet pressure and also the size of the saturator.

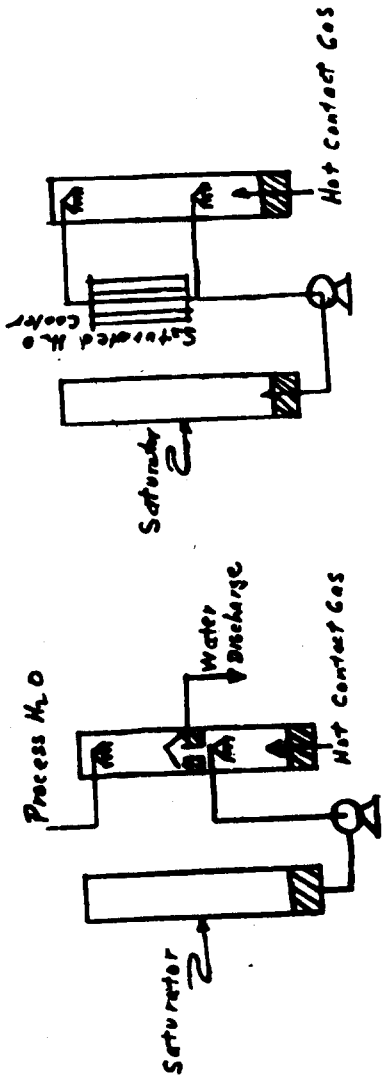
(h) In order to overcome this bottleneck, the cracked gas which formerly joined the water gas stream before the saturator, was fed directly into one of the conversion furnaces. This led to an increase in capacity because the cracking gas has a naturally higher outlet pressure, than the water gas blower, thereby reducing the load on the saturator and increasing the throughput by fifteen (15) percent. This also lowers the CO content of the feed to the CO purifier from 4.5 percent to 3.5 percent and reduces the load on the latter. It should be emphasized that as long as the cracked gas has a CO content of twelve (12) percent, the process will run on its own heat energy.

(i) Because the sulfur content of the Rhine lignite was so low, no sulfur purification was attempted on the feed to the conversion step. The sulfur content of the water gas was four hundred (400) milligrams/cubic meter (three hundred (300) milligrams H_2S and one hundred (100) milligrams organic sulfur) only slightly above the amount of purified gas in other plants. The conversion catalyst was not affected by this sulfur and ran well for three (3) years. However, the product or synthesis gas would often contain high quantities of sulfur due to the releasing of the absorbed material in the conversion catalyst bed.

(j) The reaction is



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Normal Process
Process after Installation
of the cooler

FIG. 7

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IV. WATER GAS CONVERSION UNIT. (j) (Cont'd.)

and varies with equilibrium conditions, especially the ratio of cracked gas to water gas in the feed. Hence a condition, dangerous to the hydrogenation catalyst, would occur often. Another important feature in the conversion catalytic process is the need for clean injection water, in order not to contaminate the catalyst. The minimum quantities are five (5) milligrams/liter of condensate residue and three (3) milligrams/liter of chlorine. A definite contamination was found on the top of the catalyst after three (3) years operation, even after meeting the above requirements. The deposition of solids comes only from entrainment in the saturation water and continues to build up with the addition of condensate. This addition is necessary as the saturation requires more water than is condensed in the cooler tower.

(k) By introducing a tubular cooler for the circulating saturation water, the required quantity of water injection can be reduced and an improvement in the saturator efficiency obtained. This is shown on the attached diagram (Fig. 7). In the previous arrangement, the hot exit gas was first cooled by sixty (60) degrees centigrade water and then given an after cooling of plant water. Hence the gas carried a large part of the cooling water with it which was lost.

(l) This loss was greatly reduced when the saturation water was indirectly cooled. The re-cycled water also contained less solids. It was found after a test of several weeks that the addition of fresh condensate was unnecessary and that the solid entrainment in the circulating saturation water fell below that of the plant condensate.

(m) If part of the circulating water is diverted to the lower section of the column, a two (2) degree higher saturation temperature is possible (eighty-one(81) instead of seventy-nine (79) degrees centigrade) which results in greater saturation of the gas and a considerable saving in steam requirements.

V. CO₂ PURIFICATION

(a) The unit consists of eight scrubber columns, each two (2) meters in diameter and twenty (20) meters high. In this purification step, the CO₂ content of the synthesis gas is stripped down to a trace. The operation is carried out at twenty-eight (28) atmospheres pressure.

(b) Simultaneously with the CO₂ purification, the remaining H₂S is also removed. The absorbed gases are released from the water by expansion. The quantity of wash water is fixed by the required purity from CO₂ in the synthesis gas and by the allowable combustible gas quantity in the CO₂. The process is carried out in such a way that the CO₂ content of the washed hydrogen is from 1.5 to two (2) percent, while the CO + H₂ content in this CO₂ is never above 7.5 percent. The water containing the absorbed gases is expanded in Pelton turbines which drive the fresh water pumps. The process is shown on the attached flow sheet (Fig. 8).

(c) The expansion releases eighty (80) percent of the absorbed CO₂, the inert gases and the largest part of the H₂S. The expanded CO₂ normally contains six (6) to six and one-half (6.5)