

TABLE XIX
COSTS OF OXYGEN PRODUCTION

Plant	Power to motor kwh/m ³	Power pfg/kwh	Cost of oxygen, pfg/m ³			Total
			Power	Other costs	Capital charges	
Linde	0.50	1.5	0.75	0.15	0.6	1.5
Böhlen-Brabag	0.69	1.5	1.04	—	—	3.0
Leuna	0.60	2.0	1.2	—	—	1.7-2.0
Heydebreck	—	1.4	—	—	—	2.2
Böhlen, ASW	0.9-1.0	1.1	0.9-1.0	0.4-0.5	0.9-1.0	2.2-2.5
Wanne-Eickel	—	—	—	—	—	2.3
Estimated by Koppers	—	2.0	—	—	—	2.5

using 0.67kwh/m³ for purposes of estimating in 1942. From an analysis of the figures it appears that the main reason for the higher consumptions is the rather low efficiency of the turbo-compressors, and if this could be improved up to that obtained with larger machines, then the figure might well drop to 0.5kwh/m³, as claimed by Linde.

e. Capital Cost

Information is scanty and unreliable, but the capital cost of large units appears to be of the order of RM500 per m³/hr.

f. Operating Costs

Although several figures are available, it is difficult to assess their value. Table XIX summarises the information.

Thus the achieved operating cost for big units is of the order of 2.0 to 2.5pfg/m³, with power at 1.5pfg/kwh, but the official Linde estimate appears to be low.

To translate these costs into sterling a conversion figure of RM10 = £1 might be used, but costs derived in this way should be regarded with considerable reserve.

4. SYNTHESIS GAS PRODUCTION FROM HYDROCARBON GASES

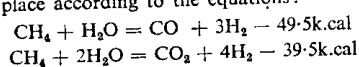
i. METHANE-STEAM PROCESS

a. General

The methane-steam process for the manufacture of hydrogen and CO from hydrocarbon gases has been widely described in pre-war technical literature, and the subject is therefore not treated in great detail in this section. Two plants of this type were installed in Germany, namely at Wesseling and at Stettin-Pölitz. The data given below refer to the achieved performance of the Wesseling plant.

b. Process

The feed gas to the methane-steam process at Wesseling consists of tail gas from the hydrogenation process. The methane-rich feed gas previously purified to a sulphur content of 5mg/m³ is mixed with steam, and passed over a nickel catalyst at 600-700°C when reaction takes place according to the equations:—



c. Equipment

The Wesseling plant consists of four units each of 66 vertical reaction tubes arranged in three groups of 22 tubes and contained in producer gas heated furnaces. The incoming hydrocarbon gas and the steam are heated to 420°C in separate heat exchangers by the outgoing reaction gas at 750°C. The producer gas used as fuel is made from brown coal briquettes, has a calorific value

of 1,450k.cal/m³, and is also similarly preheated. The hydrocarbon gas to be reacted is passed at 420°C through four catalyst chambers in series. The first is filled with iron oxide, the second zinc oxide, the third with alternate layers of iron and zinc oxides, and the fourth with spent nickel catalyst from the methane-steam reactors. Iron oxide serves mainly to catalyse the conversion of organic sulphur compounds in the feed to H₂S, zinc oxide mainly to absorb this by forming the sulphide, and the spent nickel catalyst, by promoting both these reactions, serves to bring about the final stages of purification. This treatment reduces the total sulphur content from 50mg/m³ down to 5mg/m³. Purified gas, still at a temperature of about 420°C, is joined by preheated steam, the steam/hydrocarbon gas ratio being approximately 1.2kg steam/m³ gas. The steam/hydrocarbon mixture then passes to the reaction tubes which are of Krupp's NCT6 (but NCT10 is preferred at Stettin-Pölitz). The catalyst is in ring form, 16mm × 8mm × 12.5mm.

The exit gas, which contains about 2% of residual methane, is cooled by passage through the heat exchangers, and passes to the main CO conversion plant. (See Section B5(ii).)

There are eight burners per furnace. The exit flue gases from the furnace pass first through a waste heat boiler and then through a preheater which heats the air used for combustion in the furnace. The flue gas then goes to stack. By the addition of an economiser to the waste heat boilers, the plant at Wesseling was made nearly self-supporting as regards steam. Dust in the incoming fuel gas led to trouble with the producer gas heat exchanger, necessitating a quarterly shut-down of one week for cleaning.

d. Operating Results

	1943	1944
Total cracked gas produced, m ³ /hr ..	33,600	40,000
Volume ratio of product gas to feed gas ..	2.717	2.400
Heating gas requirement, k.cal/m ³ of product gas ..	902	850
3.5ats steam required, kg/m ³ of product gas ..	0.554	0.550
18ats steam produced, kg/m ³ of product gas ..	0.320	0.450
% methane residue in product gas ..	2.7	1.5

e. References

The data on the methane-steam process collected during the course of the main missions were limited to the very brief account given in CIOS Reports XXVII—60 and XXVIII—40 on Wesseling. For the above summary, the information in the Wesseling reports has been supplemented by data supplied verbally by members of a Reparations Mission.

ii. KW PROCESS

a. General Process Description

The methane-oxygen or KW process for production of synthesis gas from hydrocarbon gases was developed

bed at 800–900°C and is interchanged with the incoming hydrocarbon gas.

With a 50% efficiency of heat exchange and when using pure methane and 98% oxygen, the overall result of this process, both chemically and thermally, is the same as would be obtained if only the following three reactions were involved:—

- (1) 98% of the methane feed reacting according to the equation:



Heat of reaction at $650^{\circ}\text{C} = 269\text{k.cal/m}^3$ of CH_4 .

- (2) 2% of methane feed reacting according to the equation:

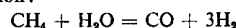
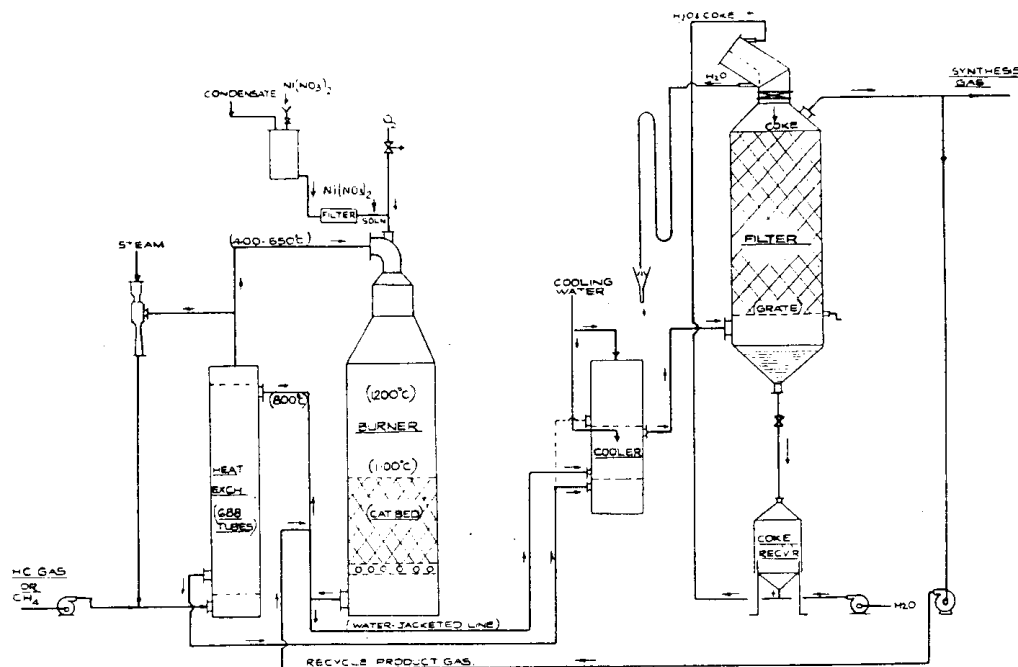


FIGURE 11



KW PLANT FOR PRODUCTION OF F-T SYNTHESIS GAS FROM HC GASES AND OXYGEN

Heat of reaction at 650°C = -2,689k.cal/m³ of CH.

(3) The reaction $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$,
proceeding to equilibrium at 850°C .

The composition of the final gas is CO_2 7%, CO 23.8%, H_2 69% and CH_4 0.2%.

The process requires a feed gas which is substantially free from sulphur, since the presence in the methane of as little as 15mg/m³ of sulphur necessitates an increase in the reaction temperature of about 200°C. It is unnecessary, on the other hand, to use a feed gas consisting entirely of hydrocarbons. Coke oven gas, or purge gas from methanol synthesis, can be treated satisfactorily. When ammonia synthesis gas is the required product, oxygen can be replaced by oxygen-enriched air.

b. Plant Operation and Details of Equipment

The following description relates to a plant treating 6,000–7,000 m³/hr of coke oven gas. A line diagram of the process is shown in Fig. 11.

Coke oven gas is introduced by means of a low-pressure blower. It first enters the tubes of a

tube and shell heat exchanger which, in the case of the Oppau plant, has 688 tubes, the upper portions of which are made of special heat-resisting alloy to contend with temperatures of the order of 800°C. The exchanger shell is fitted with baffles (9) in order to improve heat transfer. Part of the preheated gas is recycled, and the incoming steam (roughly 1 mole of steam/mole hydrocarbon in reactant gas) is injected into this recycle system. The object is to avoid condensation of water which would

occur if the steam were injected into the cold gas. The preheated gas and steam mixture, at a temperature of about 850°C, is next mixed with the oxygen or oxygen-enriched air in a mixer of the type shown in Fig. 12, which is situated at the top of the main reaction vessel. Efficient mixing of the reactants is essential for satisfactory reaction, and is achieved by introducing the preheated hydrocarbon at a pressure of 0.25–0.30ats tangentially to the stream of oxygen, which enters through

FIGURE 12

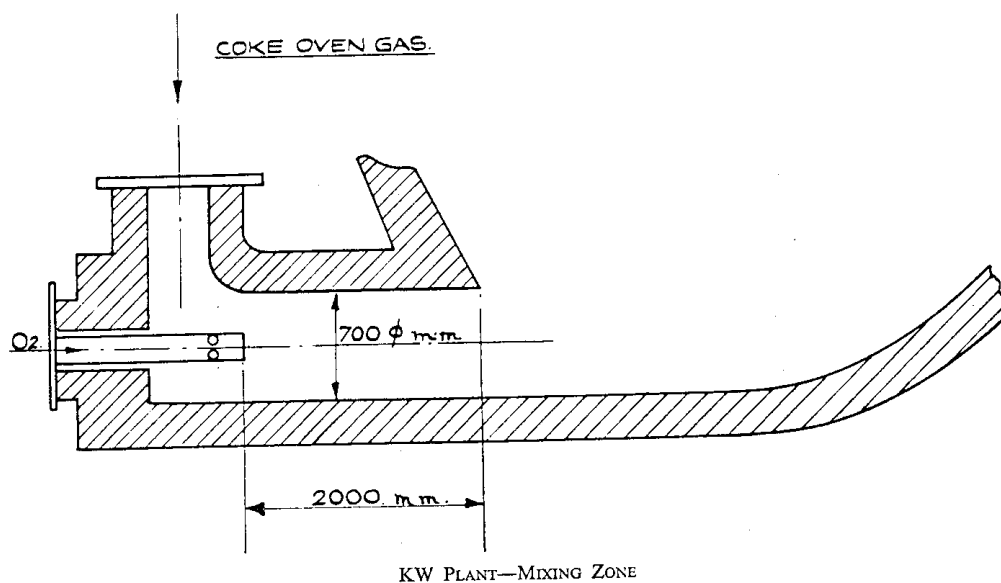
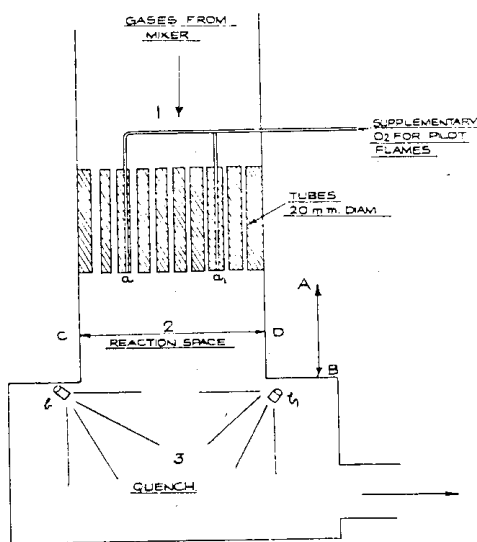


FIGURE 13



Reaction Space—Cross Section CD is $2 \times$ height AB to prevent carbon deposit; a & a₁ are O₂ leads to maintain a constant flame to start reaction; b & b₁ water jets to quench reaction. If AB is longer carbon black is formed and C₂H₂ 7–8%. With higher throughput the flame becomes unsteady. Outlets from 1 to 2 not over 20mm.

KW PLANT—ACETYLENE BURNER (SCHEMATIC)

a vertical central tube at a pressure of 0.5–0.6ats. It is claimed that mixing is complete within a length of mixing tube 1.5 times its diameter.

The mixed gases have a composition within the explosive limits, and must be protected from back-fire from the combustion zone. They are therefore separated from this zone by a bank of 20mm tubes in which the gas velocity is greater than the critical extinction velocity of the reaction, see Fig. 13.

In order to obtain uniform and complete reaction, the burner chamber which comprises the upper portion of the main reaction vessel has to be free of dead spaces where eddies can build up, and must be of such a size that the gas velocity is less than the flame extinction velocity. Pilot flames must also be provided at the entrance to the combustion chamber. These pilot flames are maintained by introducing pure oxygen through small jets uniformly placed at the exit of the flame-trap tube bank. The burner section of the reactor, which is 5.5m external diameter, is lined with 380mm of refractory material in order to withstand the temperature of 1,200–1,500°C which is reached at this stage.

The products of the combustion zone pass downwards through a catalyst bed approximately 1.8m deep and 2.75m in diameter. Loss of nickel as nickel carbonyl is replaced by introducing a solution of nickel nitrate into the combustion zone. The overall height of the complete reaction vessel is about 12m.

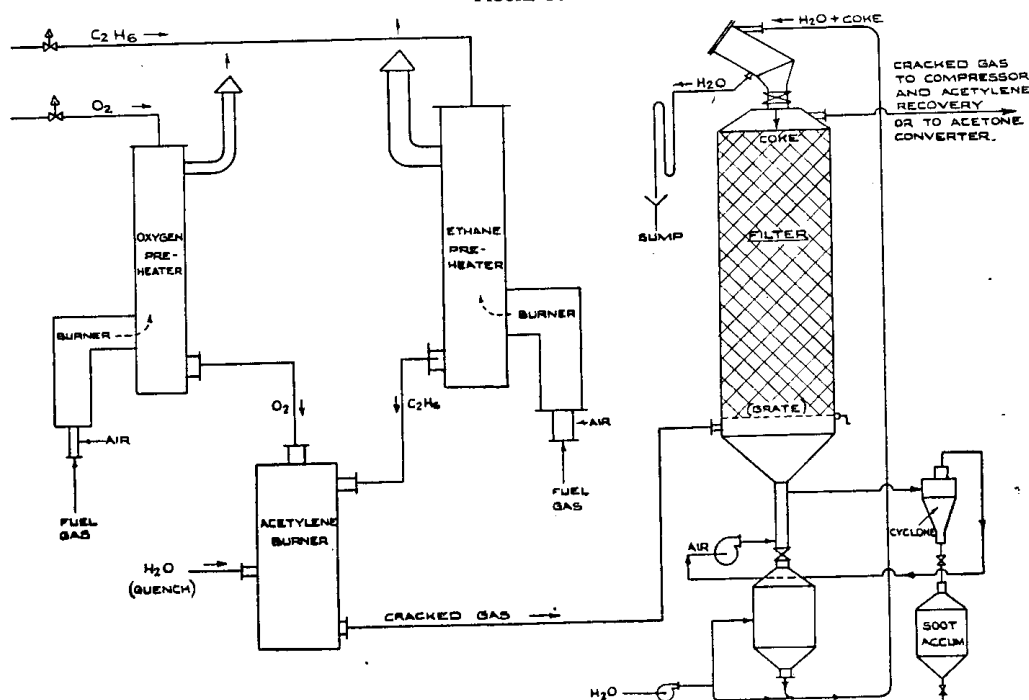
The gas leaves the catalyst bed at 800–900°C and the greater part passes to the shell of the heat exchanger. Exit gas from the exchanger at a temperature of 350°C

of the burning stage of the normal KW gas process, with the addition that the products of combustion are cooled very rapidly by water quenching. The reaction chamber has to be small enough and the mixing of the reactants sufficiently efficient to ensure that the duration of the burning reaction does not exceed one-hundredth of a second. A line diagram of the process is shown in Fig. 14.

Both the hydrocarbon gas and the oxygen have to be preheated to 400°C in gas-fired heaters. When using methane as the feed, the ratio hydrocarbon : oxygen is 2 : 1. No steam is introduced with the reactant gases.

The reaction vessel consists of a mixer, a combustion section and a water quenching arrangement. The very

FIGURE 14



KW PLANT FOR PRODUCTION OF ACETYLENE FROM ETHANE AND OXYGEN

efficient mixing which is necessary is obtained by adding a second bank of flame-trap tubes. The two tube banks are separated by a very small space and are arranged so that the orifices are staggered, see Fig. 15. The burning zone has generally a diameter of 700mm and a length of 350mm, and the gas velocity through this zone is 8.5m/sec. A temperature of around 1,500°C is reached.

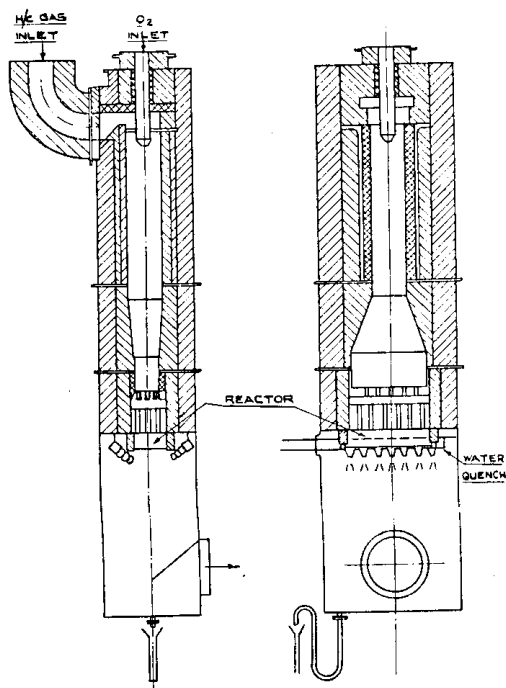
The water sprays cool the reacted gases to 80–90°C, after which they are passed to a coke filter for removal of soot and tarry matter. This part of the apparatus is identical to that used for synthesis gas production except that soot is removed from the spent coke by air blowing instead of by water treatment. Soot is recovered from the circulating air by means of a cyclone.

When using methane as a raw material, the gas leaving the scrubber contains 8-9% acetylene, 3-4% CO₂, 6-7% methane, 24-26% CO and 56% H₂.

When concentrated acetylene is required, this exit gas is compressed to 18ats, and washed with water. The solution of gases in water is let down in two stages:

Substantially 100% hydrocarbon gas and pure oxygen are necessary for this process. It consists essentially

FIGURE 15



KW PLANT—ACETYLENE BURNER (DETAIL)

(a) to 3ats, the gas evolved being recycled to the compressor; and (b) to 1·1ats. Before recycle the wash water is degassed under a vacuum of 0·05ats. Gases obtained in the second let down and in the degassing operation are mixed and this final product contains roughly 70% acetylene and 28% CO₂.

Gas leaving the water washer at 18ats contains 50–60% H₂, 35–40% CO and 6–8% CH₄. If this gas has too great a methane content for synthesis purposes, it is given a second oxygen burning treatment. This is apparently carried out without steam and in a unit containing no catalyst bed. There are also indications that this second stage burning may be carried out under pressure of 18–30ats.

A flow diagram for the acetylene concentration method is shown in Fig. 16. This is a summary flowsheet of the proposed Heydebreck operation using ethane as raw material, and in addition to the acetylene concentration steps, it provides data on the secondary combustion of the synthesis gas.

An estimate of the costs of acetylene production from ethane was made by the IG in connection with the proposed Heydebreck plant.

The capital cost and production cost for a plant to produce 1tc/hr acetylene, together with 10,000m³/hr of synthesis gas was calculated to be RM2,000,000, made up as shown in Table XX.

iv. KOPPERS PROCESS

a. General

A process has been developed by Koppers for producing hydrogen from coke oven gas by reacting the hydrocarbons therein contained with steam. The

FIGURE 16

PROPOSED FLOW PLAN OF HEYDEBRECK ACETYLENE OPERATION

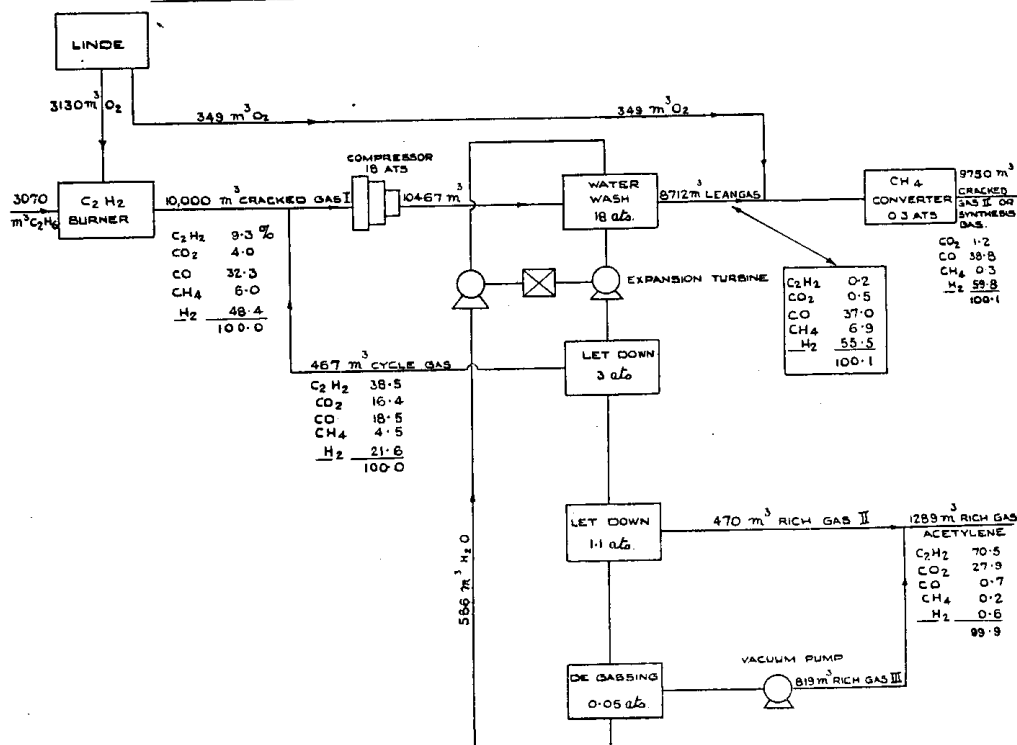
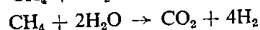
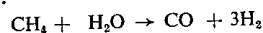


TABLE XX
COSTS OF COMBINED ACETYLENE AND SYNTHESIS GAS PRODUCTION

CAPITAL COST OF ACETYLENE GENERATION:—			
Acetylene generators (5 units)	RM700,000		
Compressors for acetylene concentration	600,000		
Acetylene scrubbing plant	400,000		
Secondary treatment of synthesis gas with oxygen	300,000		
			2,000,000
PRODUCTION COSTS ESTIMATED:—			
Ethane, 3,070m ³ /hr at 0.71 pfg/1,000k.cal	RM/hr307.00		
Acetylene synthesis costs:—			
Oxygen, 3,130m ³ /hr at 2.2pfg/m ³	RM/hr68.20		
Fuel gas, 1.67 × 10 ⁶ k.cal at 0.45pfg/1,000k.cal	7.55		
Electric power, 120kwh at RM0.014	1.68		
Cooling water, 160m ³ at RM0.02/m ³	3.20		
Wages, 5 man-hours at RM2.40, including 50% oncost	12.00		
Repairs			
Amortisation } 18% on capital value	14.50		
Taxes, etc.			414.13
Acetylene concentration:—			
Electric power, 1900kwh at 1.4pfg/kwh	26.60		
Cooling and wash water, 300m ³ /hr at 2.0pfg/m ³	6.00		
Lube oil, 1kg/hr at 50pfg/kg	0.50		
Wages, etc., 3 man-hours at RM2.40, including 50% oncost	7.20		
Repairs			
Amortisation } 18% on capital value	20.70		
Taxes, etc.			61.00
Secondary treatment of synthesis gas:—			
Oxygen, 349m ³ /hr at 2.2pfg/m ³	7.70		
Cooling water, 30m ³ /hr at RM0.02/m ³	0.60		
Wages, 2 man-hours at RM2.40, including 50% oncost	4.80		
Repairs			
Amortisation } 18% on capital value	6.20		
Taxes, etc.			19.30
			494.43
TOTAL			264.00
Credits 9,750m ³ /hr synthesis gas at 2.7pfg/m ³ *			230.43
Cost of 0.975te acetylene			RM/te 236.00
Acetylene cost			

* Oppau cost at end of 1939.

reactions are similar to those used in the methane-steam process, viz:—



Both of these reactions are endothermic, but whereas in the methane-steam process the necessary heat is passed through tubes of special steel containing the catalyst, in the Koppers process the heat is imparted to the reactants by passage through large vessels containing chequer refractory materials—"Cowpers." The "Cowpers" are heated by burning gas, and air in the reverse direction. There is no catalyst, except possibly the chequer brick-work itself, and therefore the reaction temperature is much higher than with the methane-steam process.

b. Plant Location

The plants concerned are at Castrop-Rauxel, and at Rheinpreussen. Information on the latter plant is scanty, and the following data are therefore derived chiefly from the Castrop-Rauxel installation. The plant was not actually of Koppers design, but was similar in principle, and was said to give a comparable performance.

c. Equipment

The Castrop-Rauxel plant consists of four large steel towers, arranged in two pairs of two, heavily lined with refractory brick, and filled with refractory chequer brick.

The dimensions of these "Cowpers" are given in the attached sketch (Fig. 17), but those at Rheinpreussen were apparently bigger. Before passing to the cracking chambers, the coke oven gas passes through a tower, where it is saturated with water vapour at 70°C.

d. Process

A 15-minute cycle is employed: 7min heating by combustion of Fischer tail gas, flue gas to stack; 0.25min "blow-purge," with coke oven gas, but exit gases to stack; 7min "run" with collection of cracked gas; and 0.75min "run-purge" using combustion gas, but with exit gas to collecting main.

The temperature of the chequer work is variously reported as 1,350–1,400°, 1,300° and 1,450°C.

e. Outputs and Efficiencies

At Castrop-Rauxel the twin pairs of ovens together deal with 6,000m³/hr coke oven gas containing 22–25% CH₄, and of 4,200k.cal/m³ calorific value.

The make gas has the following % composition:—

H ₂	CO	CO ₂	CH ₄	N ₂
73	4–5	2–3	3–5	7–8

The make gas also contains 7gm/m³ of carbon which is removed by water scrubbing, and is filtered out and used as a rubber filler.

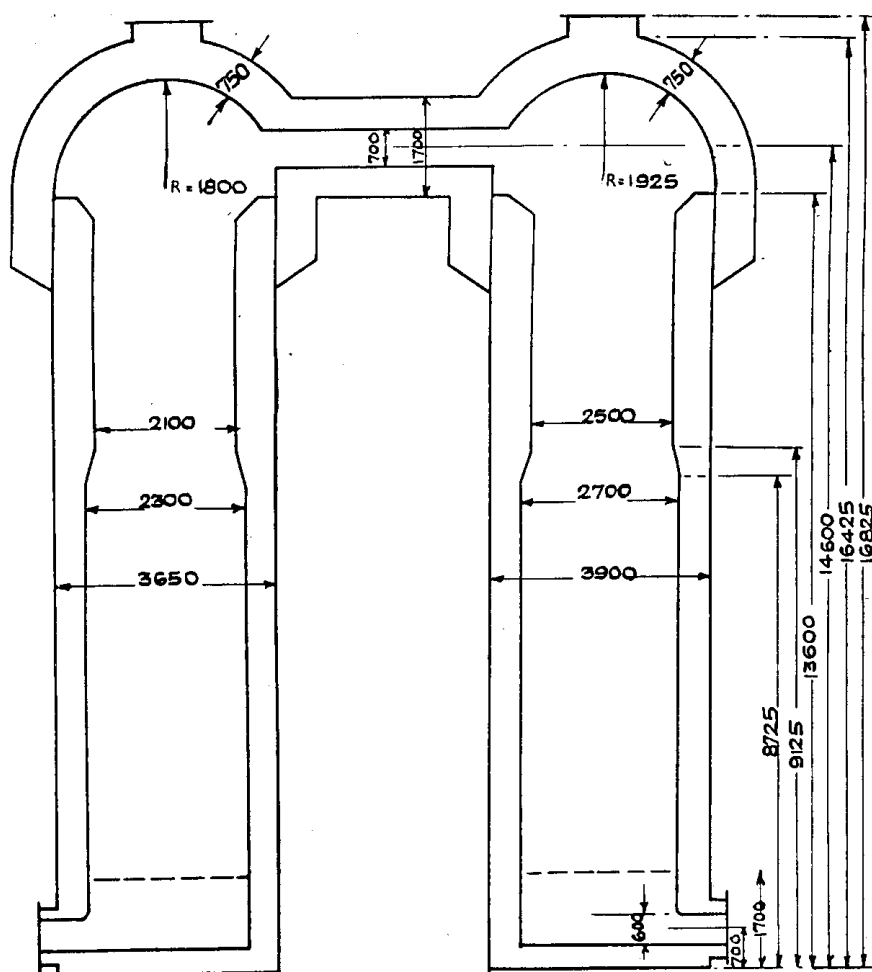
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The total steam consumption is $3.5 \text{ te/hr} = 0.58 \text{ kg/m}^3$ coke oven gas. Gas from a water saturator operating at 70°C would contain about 0.28 kg steam per m^3 dry gas, but whether the above steam quantity includes this amount is not clear.

Per m^3 of inlet coke oven gas:—

Exit gas volume	...	1.8 m^3
Steam	...	0.9 kg
Fuel gas	...	1,515 kcal
" " calorific value	...	2,500 kcal/m^3

FIGURE 17



All dimensions in millimetres

COKE OVEN GAS CRACKING PLANT—GEWERKSCHAFT VICTOR, CASTROP-RAUXEL

The exit gas volume is not stated in any reports, nor is it possible to calculate it with certainty, but it looks as if it should be about 1.5 vols cracked gas per unit volume of coke oven gas.

The fuel gas requirement is $2,000 \text{ m}^3/\text{hr}$ of gas of calorific value $2,500 \text{ kcal/m}^3$, that is, 830 kcal/m^3 of coke oven gas.

The above figures should be used in assessing the economic value of the process since they are achieved results. It should, however, be noted that the Koppers Company themselves claimed a plant with the following improved figures (see Fig. 18), but it is not clear whether these results were achieved or expected:—

Exit gas	H_2	CO	CO_2	CH_4	N_2
	69.1	19.7	5.1	1.0	5.1

5. CONVERSION OF WATER GAS TO HYDROGEN OR FISCHER SYNTHESIS GAS

i. H_2S REMOVAL

a. General

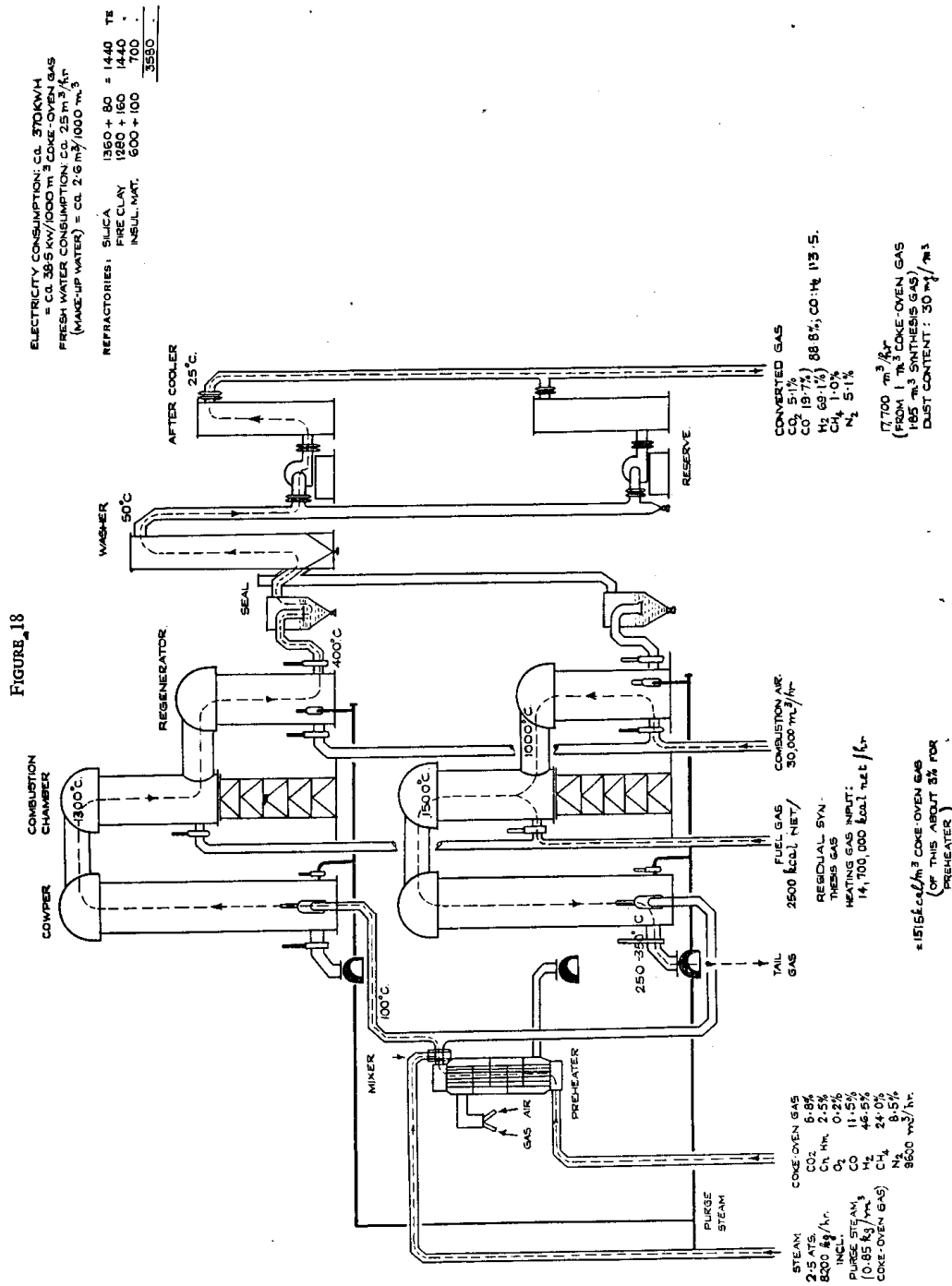
The first step in the conversion of water gas into hydrogen or in its use as a component of Fischer synthesis gas, is usually removal of hydrogen sulphide (H_2S). The conventional method is to absorb the H_2S by hydrated oxides of iron at substantially atmospheric temperature and pressure. The process, although used extensively in Germany, is so well known that it is not proposed to deal with it in this report. A rather less known process in considerable use in Germany is the so-called Alkacid process. At Leuna, the water gas is purified from H_2S by oxidation over active carbon to sulphur and water.

b. Alkaid Process

In this process the gas is washed with a solution of a salt of an amino-acid which is regenerated by steam.

At the IG Farbenindustrie Works at Leuna, purification of water gas made in Winkler generators was carried out with a solution of sodium glyccoll,

($\text{NH}_2\text{CH}_2\text{COONa}$), of sp.gr. 1.17, containing 200gm/litre calculated as Na_2CO_3 , or 45gm/litre calculated as N_2 . Sodium glyccoll is a selective absorbent for H_2S , so that with a gas containing 20% CO_2 and 2% H_2S it will remove nearly all the H_2S , but only about 2% CO_2 . Another substance used at Leuna was sodium alanine, ($\text{CH}_3\text{CH}(\text{NH}_2)\text{COONa}$), but this dissolves CO_2 also.



It was used only for the purification of the tail gases from hydrogenation. At the high pressure hydrogenation plant at Wesseling, the potassium salt of dimethyl-amino-acetic acid, $((\text{CH}_3)_2\text{N}.\text{CH}_2.\text{COOK})$, was used under the name of "DIK Liquor" as a selective absorbent for H_2S . The potassium salt of methyl-amino-propionic acid, $\text{CH}_3.\text{CH}(\text{NH}.\text{CH}_3).\text{COOK}$, was used under the name of "M Liquor" to absorb both H_2S and CO_2 . The water gas from the Winkler generators at Brabag I Plant, Böhlen, was washed with "DIK Liquor."

It was stated at Leuna that sodium glycol and sodium alanine are as efficient as ethanolamine as regards absorptive capacity, regenerative capacity and stability, while they are superior as regards purification to low concentrations and non-volatility. Severe corrosion difficulties were experienced at first, but laboratory research showed that while concentrated solutions of sodium alanine do not attack aluminium, solutions of sp.gr 1.12 or less do attack the metal. As a result, the works plant was operated with a solution which was not allowed to fall below a sp.gr of 1.16, and no corrosion difficulties were experienced. Similarly, at Wesseling the sp.gr of the solution was kept at 1.155 by control of the relative amounts of direct and indirect steam used for regenerating the liquor. At Böhlen the "DIK Liquor" sp.gr was maintained at 1.165. The plant at Leuna used iron for the cold plants, brick-lined iron for the regenerator, aluminium for the indirect heater and hot pipes, and an aluminium-silicon alloy called Silumin or Alpac for the pumps. At Böhlen the scrubber was made of iron, the rings of earthenware, and the regenerator, pumps and distributor of aluminium. Corrosion was slight, but it has been intended to replace the regenerator by one built of V2A steel. A recent DIN specification for Alkazid plants recommended ordinary steel or iron up to 50°C , 17% chromium steel up to 95°C and a ferrous alloy containing 18% chromium and 9% nickel with a small amount of carbon for boiling solutions.

The Alkazid system is as follows. The cooled washing liquor is passed down the absorber counter current to the gas. The quantity of liquor required depends on the hydrogen sulphide content of the gas and the washing temperature. At Leuna, using sodium glycol for H_2S removal, there is required 1 volume of liquor to 1,500 volumes of gas in winter, and 1 volume of liquor to 500 volumes of gas in summer. The absorbers at Leuna consisted of vessels of 3m diameter for a gas throughput of $20,000\text{m}^3/\text{hr}$, containing 7 to 9 bubble cap trays. The absorbers at Wesseling were of a similar type, but those at Böhlen were packed with rings. The solution is then pumped through heat exchangers to the top of the regenerators. The regenerator is a ring-packed column, into the base of which direct steam is introduced to drive off the H_2S in the foul liquor. Indirect steam is also used by circulating liquor by natural convection through a tubular heater connected across two points in the lower part of the regenerator. The hot regenerated liquor passes through the heat exchangers to coolers, and then returns to the absorbers. The mixture of H_2S , CO_2 and H_2O vapour leaving the regenerator is condensed at $50\text{--}60^\circ\text{C}$ in order to reduce the H_2S content of the condensate and the H_2S and CO_2 gases then pass to a Claus kiln for production of sulphur of 99.6–99.9% purity.

The Winkler gas at Leuna contained $15\text{--}20\text{gm H}_2\text{S}/\text{m}^3$. It was washed in a two-stage Alkazid plant. In the first stage the concentration of H_2S was reduced to $2\text{gm}/\text{m}^3$, using 80kg of steam per m^3 of liquor in the regenerators. In the second stage the H_2S was reduced to $150\text{mg}/\text{m}^3$, using 150kg of steam per m^3 of liquor.

The HCN present in the gas should be removed before it enters the Alkazid plant in order to avoid loss of the absorbent as NaCNS or KCNS . Laboratory experiments were carried out with fresh iron oxide, spent iron oxide, iron sulphate solution, sodium polysulphide solution and active carbon. It was decided that potassium carbonate solution was more suitable than any of these, and the process was installed at Leuna and Böhlen.

The gas is washed in a tower packed with rings or wooden grids (the former being preferred) with a 10–15% solution of K_2CO_3 , using 1 volume of solution to 300 volumes of gas. 10% of the circulating liquor is withdrawn continuously, heated to 80°C and passed over sulphur to form KCNS . This solution is then cooled and returned to the circulating liquid. The strength of the circulating liquor is maintained by evaporating off the water condensed from the gas. Liquor is discarded from the system as required in order to maintain a convenient concentration of thiocyanate, and the discard is made up by adding fresh K_2CO_3 solution. The HCN in the gas is reduced by this process from $12\text{--}14\text{mg}/\text{m}^3$ to $1\text{--}2\text{mg}/\text{m}^3$.

It was customary to follow the Alkazid plant with iron oxide boxes containing luxmasse for the final purification of synthesis gas from hydrogen sulphide.

Sodium alanine can be used to remove carbon dioxide from gas, when its capacity (used in the same concentration as with glycol) amounts to $25\text{m}^3 \text{CO}_2$ per m^3 of liquor, the steam consumption for regeneration being $120\text{kg}/\text{m}^3$ of liquor. Over 95% removal of CO_2 is possible.

c. Purification by Active Carbon

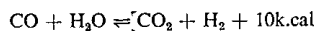
The whole of the water gas made in the Pintsch-Brassart generators at Leuna, amounting to $240,000\text{m}^3/\text{hr}$, together with some of the part-purified Winkler gas led off after the first stage of the Alkazid plant, was purified by means of active carbon, reducing the H_2S content from $3\text{--}4\text{gm}/\text{m}^3$ to $1\text{--}2\text{mg}/\text{m}^3$. Crude Winkler gas could not be purified by active carbon because its high content of hydrogen sulphide caused excessive temperature rise.

The carbon was prepared from brown coal carbonised at 900°C and then steamed. Air or oxygen was added to the inlet gas, so that H_2S was oxidised to sulphur, which was left on the carbon. NH_3 was added to the gas to act as a catalyst. After gas had been passed for about ten days, the sulphur was extracted with ammonium sulphide solution at 40°C in the absence of air. The polysulphide solution was then distilled at 2ats, with a top temperature of 111°C . The vapours were condensed and used again, while molten sulphur and liquid water separated into two layers at the bottom of the still and were run off. It was stated that the still effluent was not obnoxious.

ii. HYDROGEN PRODUCTION BY CARBON MONOXIDE CONVERSION REACTION

a. Normal Process

General.—Equipment for carrying out the so-called water gas reaction:—

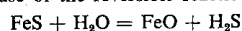


has been widely described in pre-war literature.

In the conventional atmospheric pressure process, the reaction is normally carried out in two stages, the first being at a higher temperature than the second, to give a rapid initial reaction. In the second stage, the lower temperature gives a more favourable equilibrium and the reaction proceeds further. The temperature range

is usually 500–400°C, therefore the hot out-going gas is heat exchanged with the inlet gas. Some of the heat of reaction is recovered by counter-current scrubbing the hot exit gas with water, and using this hot water to saturate the inlet gases.

Plant at Wesseling.—It will be seen from Fig. 19 that this is a typical orthodox plant; cooling between the two stages of conversion is by water spray which, of course, also provides additional steam. Normally, H_2S is removed from water gas used in the CO conversion process, but at Wesseling the S content of the brown coal used is so low that this step is dispensed with. This has sometimes led to trouble with high H_2S in the exit gas because of the reversible reaction:—



i.e. increase in inlet steam would cause H_2S evolution.

The sulphur content of the inlet gas (300mg H_2S + 100mg organic sulphur per m^3) causes no deterioration of the catalyst activity.

The solids content of the water injected between the two stages must be low (<5mg/litre with <3mg/litre of

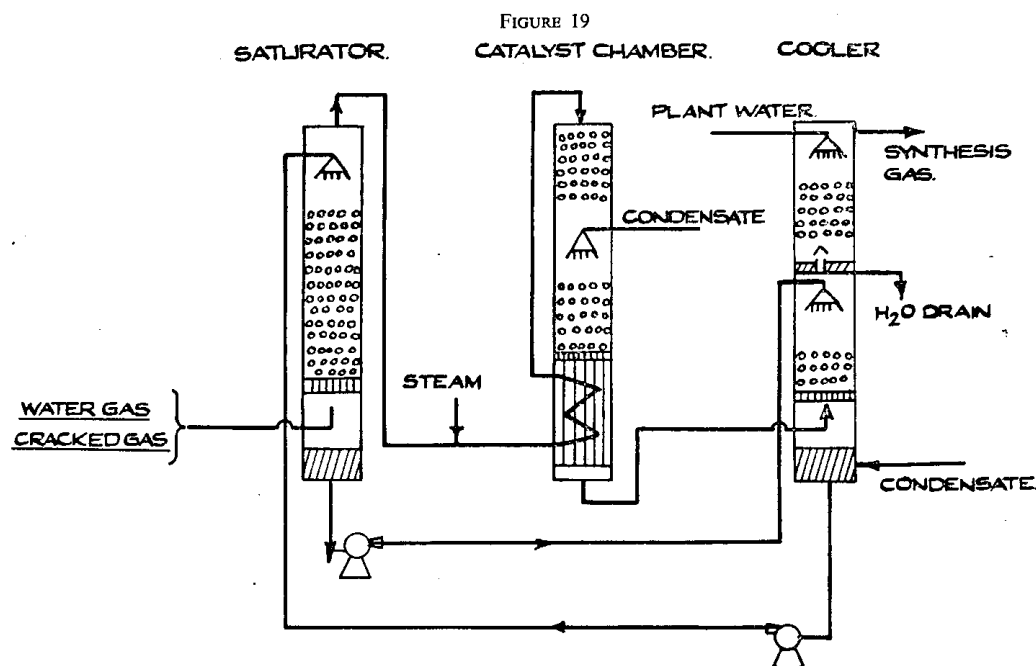
chlorine). The most satisfactory water for this purpose is the condensate obtained by indirect cooling of some of the exit gas, instead of passing it to the direct contact cooler.

It has been found that the temperature of the exit saturated gas from the saturator can be raised from the usual 79°C to 81°C by injecting some of the hot water from the water heating tower half way down the saturator.

Gas from the methane-steam units (see sub-section 4 (i) of this Section, p. 28) is added before the converters.

b. Pressure Process

Processes for the conversion of CO to hydrogen under pressure of about 30ats were developed in Germany during the war principally by IG and by Bamag. The following information was obtained from Dr. Schierenbeck, who had been in charge of the IG work and from the engineer responsible for the installation of the plant at Blechhammer. The pressure process had been adopted extensively for the new plants in the East of Germany during the war.



WESSELING PLANT FOR CARBON MONOXIDE CONVERSION

TABLE XXI
OPERATING DATA FOR CO CONVERSION AT WESSELING

		1943	1944
Total exit gas rate	m^3 dry gas/hr	103,000	120,000
Inlet gas rate/two-stage converter	" "	7,000	7,200
CO in inlet gas	%	24.9	26.4
CO in exit gas	%	4.1	4.4
Ratio of exit to inlet gas		1.202	1.205
Steam in inlet gas from saturator	kg/ m^3 dry gas	0.274	0.25
Live steam added	" "	0.187	0.22
Condensate added at interstage	" "	0.015	0.020
Steam introduced with methane-steam gas	" "	0.118	0.100
Total water vapour	" "	0.594	0.590

Theoretically there are sound reasons for the use of a pressure process. The final products have in any case to be compressed for the removal of carbon dioxide and, since the reaction $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ gives a 100% increase in volume of permanent gases, operation under pressure eliminates compression charges in respect of the newly-formed carbon dioxide. As far as compression is concerned there is clearly no advantage to be gained by use of a pressure higher than that to be employed for carbon dioxide removal.

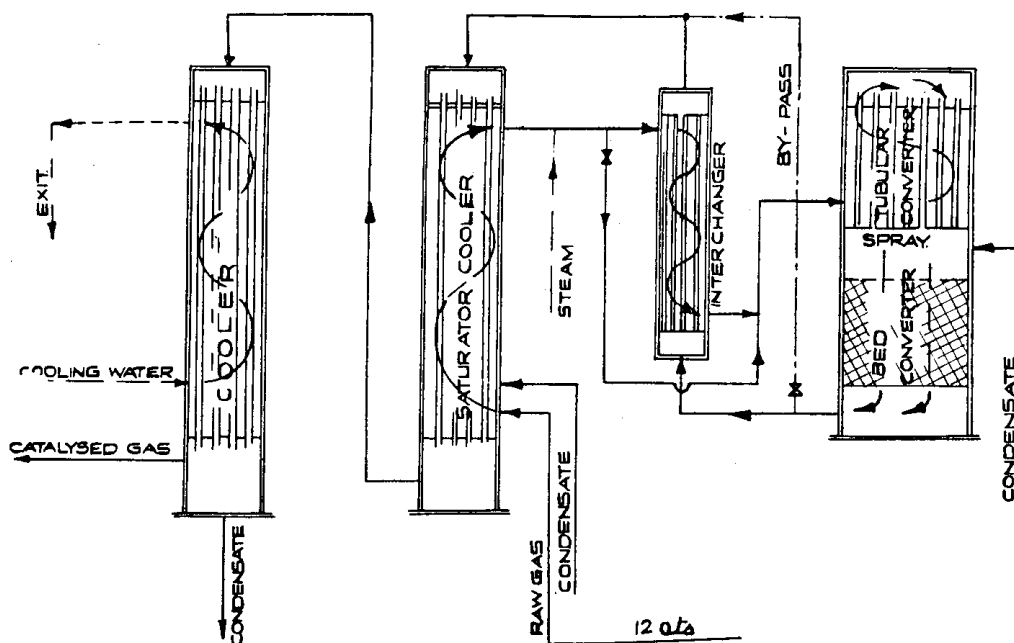
Secondly, although the equilibrium of the reaction is unaffected by pressure, enhanced pressure increases the volume of gas (measured at NTP) which can be treated in a plant of given size and catalyst capacity. No

The potential disadvantage of the pressure process is corrosion due to an increased concentration of dissolved carbon dioxide, oxygen and sulphur gases in the water.

The pressure plant developed by IG attempts to secure all three of the above advantages. A flow diagram of the plant is shown in Fig. 20 and, for comparison, Fig. 21 illustrates a typical low pressure unit.

The feed gas under a pressure of 12-30ats together with condensate water is introduced to the shell of a tube interchanger (40mm tube diam.) where it absorbs heat from the exit gas from the process and becomes saturated with water vapour. This heat exchanger takes the place of the direct water heater and the saturator

FIGURE 20



SCHIERENBECK SYSTEM—BLECHHAMMER

change in reaction temperature and no special catalyst is necessary. The IG use a catalyst consisting of 91% Fe_2O_3 and 7% chrome oxide, as in atmospheric units.

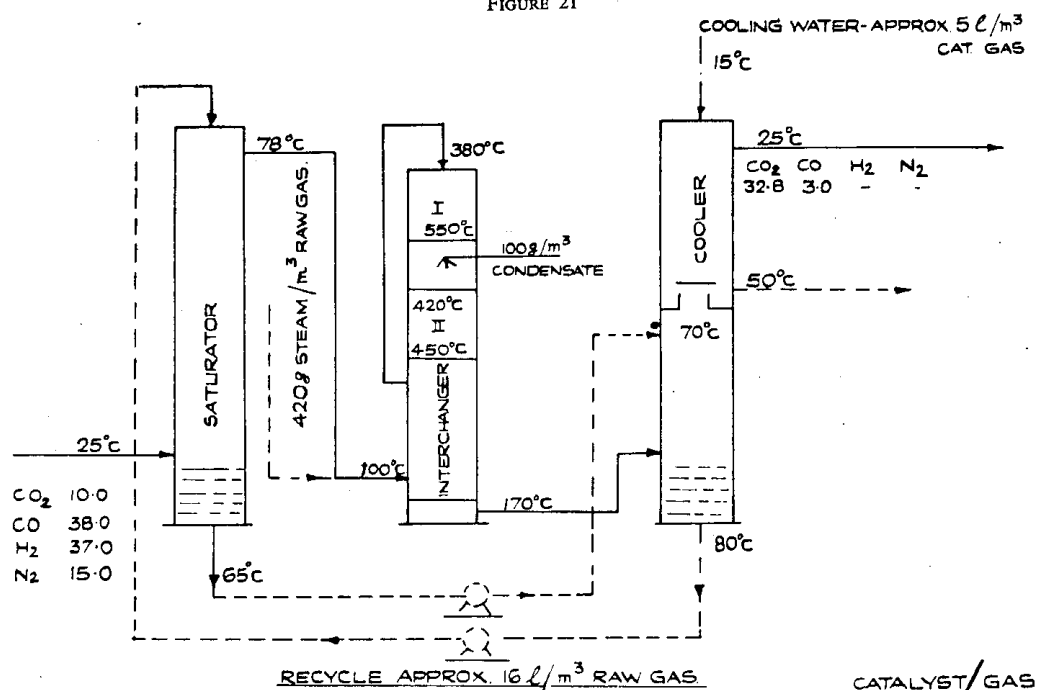
The increase in unit capacity was particularly attractive for Germany during the war because of the resulting economy in steel, but as will be seen later, the advantage has been offset by the necessity to use special steels for the pressure process.

The third potential advantage of pressure operation is the economy in steam. Under normal atmospheric pressure conditions, one of the chief heat losses from the process results from the comparatively large quantity of water vapour carried away by the exit gases from the water heater and condensed in the final cooler (see Fig. 21). Provided that use of increased pressure is not accompanied by an increase in exit temperature of the final gases, it will reduce this loss of water vapour, and therefore the heat loss, because of the reduction in volume of exit gas. In addition, the general heat losses from the system (per m^3 of gas product) should be reduced by the increase in unit capacity.

vessel used in atmospheric pressure plants. The efficiency of the interchanger is controlled by varying the level of water held in the shell, thereby varying the amount of tube surface available for interchange. The latest IG design for this saturator-heater employs flattened tubes of 4mm/60mm cross-section, it being claimed that tubes of this shape result in a saving of steel and in equal heat transfer coefficients on both sides of the tubes. Individual tubes are separated by a space of about 4mm.

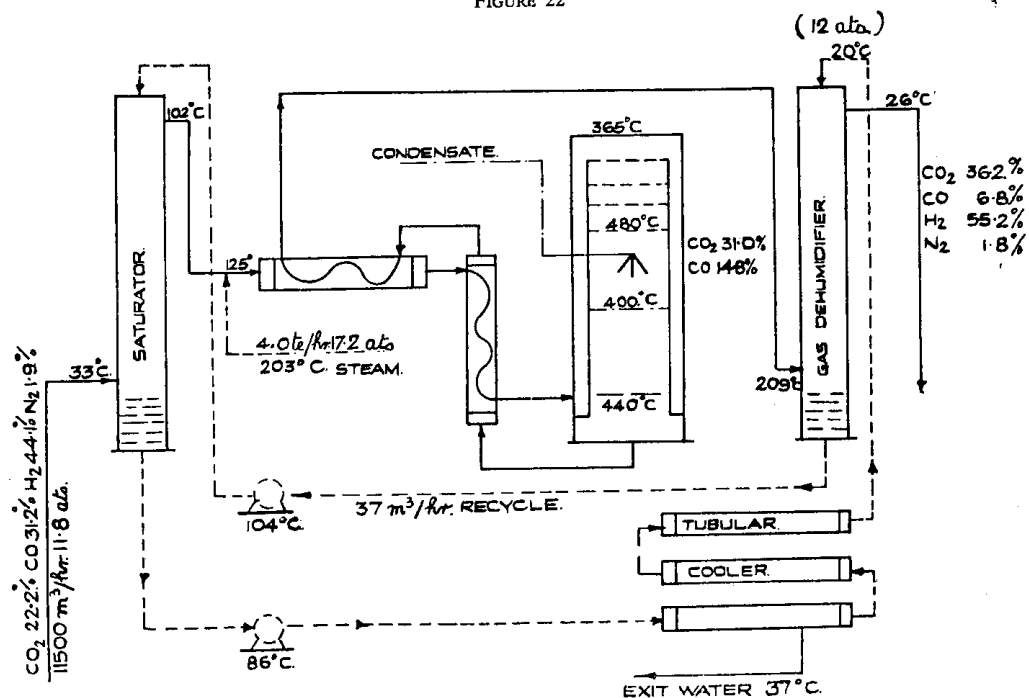
The partially preheated saturated gas is joined by make-up steam and passes to the main interchanger where it is heated to about 380°C . It then passes to the upper reaction zone of the converter which consists of a bank of tubes containing catalyst. The incoming gas first travels upwards outside the tubes and is heated to 450°C , after which it passes downwards through the catalyst tubes. Heat is generated during reaction, but is simultaneously absorbed by interchange with the inlet gas. The result is that the temperature of the reactant gases in the tubes first rises to about 500°C

FIGURE 21



LOW-PRESSURE CO CONVERSION—LEUNA

FIGURE 22



PRESSURE CO CONVERSION—BRUX

and then falls gradually to about 400°C at the exit of the upper reaction zone.

Before passing to the second part of the reaction vessel, which consists of a normal catalyst bed, additional water condensate is introduced as a spray. The final gas product leaves the bottom of the reactor at about 440°C, and travels through the tubes of the two interchangers to a final indirect water cooler.

An alternative design of pressure plant developed by Bamag is shown in Fig. 22. The separate water heater and inlet gas saturator employed in atmospheric pressure units are retained. The main change is that the final indirect water cooler is used to cool the water condensate recycled from the saturator to the water heater. In this way the water heater becomes the final cooler for the exit gas.

It was stated that, in some Bamag designs, the second interchanger (shown in Fig. 22, in use for preliminary preheat of saturated inlet gas) is used to preheat water passing from the water heater to the saturator.

In order to combat the corrosion problem, the parts of a pressure plant with which liquid water is likely to come into contact should be made of special steel. IG at Oppau prefer to use 17% chrome steel, but have used V2A and occasionally FF6N 6% chrome steel. For the new flat tube saturator-heater, it is proposed to use Sicromal 8 (5% chrome, 1% silica).

Pressure conversion units are reported to have been erected at the following factories:—

Oppau	IG design	25ats
Blechhammer ..	" "	12.5ats
Heydebreck ..	" "	30ats
Auschwitz ..	" "	21ats
Brüx	Bamag "	12.5ats
Linz	IG "	30ats
Lützkendorf ..	Bamag "	8ats

With a catalyst volume of 10m³, a 25–30ats pressure plant has a capacity of 25,000m³/hr inlet gas. An atmospheric pressure unit of the same catalyst volume will treat only 3,000m³/hr. Dr. Schierenbeck was of the opinion that it would not be practicable to build an atmospheric unit with a capacity of more than 10,000m³/hr inlet gas.

It is unlikely that this increase in unit capacity results in any appreciable reduction in capital cost per m³ of synthesis gas product, (a) because of the necessity for special steels and (b) because, generally, the use of high-capacity units means that a bigger percentage spare capacity has to be installed. For regular production of 100,000m³/hr synthesis gas, five pressure units with a total capacity of 125,000m³/hr would have to be installed, compared with, say, 11 atmospheric units with a total capacity of 110,000m³/hr.

On the operating side there should be a saving in labour and repairs, but the former will be small, because labour requirements for any type of water gas shift plant are extremely low, and the latter can easily be offset by increased cost of replacement materials in the event that any appreciable corrosion takes place.

Oppau claim that the requirement of make-up steam when using the 25–30ats process is only 250gm/m³ of inlet gas, compared with 400gm for the atmospheric pressure process. IG seem to set great store by the steam saving, and this is rather surprising in view of its relatively small influence on cost, particularly when the process is operated at a factory where HP steam has a premium value.

The main saving effected by the pressure process

appears to be the reduction in compression charges, which, of course, is considerably greater when hydrogen or ammonia synthesis gas is the required product, than is the case when synthesis gas for methanol or the Fischer-Tropsch process is being made.

IG at Oppau continue to be enthusiastic about the merits of the pressure process, and claim that its operation at Oppau has saved the capital cost of the new plant in 3 to 4 years. The managements of the new plants in Eastern Germany, on the other hand, are dissatisfied with the process, and the Brüx and Blechhammer staff feel that troubles experienced with the pressure shift plants have limited the output of the main plant. Corrosion troubles have been frequent and severe on all these plants, but they have certainly been aggravated by attempts to use inferior materials because of the shortage of special steels. Trouble has also been experienced with short catalyst life, but this again has probably been largely a secondary effect of corrosion, scale from the plant being deposited on the catalyst. Bombing may also have contributed to this trouble in a number of cases; for example, gas lines have been damaged and dust introduced into the plant.

A good deal of the trouble experienced at Blechhammer was caused by a definite mistake in design. All the preliminary design work was carried out on the assumption that the plant would operate at 30ats, and it was only in the late manufacturing stages that it was realised that the plant was to operate at 12½ats. In order to reduce the pressure drop across the unit, various interchanger tube bundles and the catalyst beds were cut in two and arranged for operation in parallel. This apparently led to a reduction in heat efficiency of the unit.

iii. REMOVAL OF CARBON DIOXIDE AND CARBON MONOXIDE FROM SYNTHESIS GAS

a. Carbon Dioxide Removal

The removal of carbon dioxide from the product gas from the carbon monoxide conversion stage is normally carried out by water scrubbing. The process, as carried out in the Wesseling, Böhlen and Leuna hydrogen production plants, was examined in detail. The operating pressure at the first two plants was 28ats and at Leuna, 25ats. The dissolved gases are released from the wash water by reducing the pressure to atmospheric.

In addition to carbon dioxide, the water dissolves substantially all the hydrogen sulphide formed from organic sulphur compounds during the carbon monoxide conversion reaction. It also dissolves some hydrogen, carbon monoxide, methane and nitrogen, according to the partial pressures of these components in the gas. The quantity of water used is determined by the required degree of removal of carbon dioxide, and the permissible content of combustible gases in the recovered carbon dioxide.

At the high pressure hydrogenation plant at Wesseling, the purification plant was so operated that the CO₂ content of the washed synthesis gas was between 1.5 and 2.0%, while the H₂ + CO content of the CO₂ evolved on reducing the pressure on the wash water was maintained below 7.5%. The H₂S in the CO₂ evolved was about 500mg/m³. The average water circulation rate was 40m³/1,000m³ inlet gas.

The Wesseling plant had eight scrubbers, each 2m in diameter and 20m high, packed with 60mm earthenware rings, for a gas throughput of 120,000m³/hr. The Brabag I plant at Böhlen had seven towers, each of 1.75m internal diameter at the bottom and 1.44m at

the top, of total height 18m, packed 12-14m with two sections of 50 × 50mm rings. Each tower washed 8,000m³/hr of gas, using a washing ratio of 30m³/1,000m³ in winter with water at 10°C, rising to 60m³/1,000m³ in summer with water at 20-27°C. The CO₂ in the gas was reduced from 40% to 1.6%.

The water leaving the scrubbers was expanded through Pelton turbines coupled to water pumps, when about 80% of the dissolved CO₂ was evolved. The water was then freed from its residual CO₂ and H₂S by blowing air through it. A portion was re-used for CO₂ scrubbing, and the rest was pumped to the works water system. The purpose of re-using the aerated water in the CO₂ scrubbers was to introduce a definite quantity of oxygen into the crude hydrogen, so that in the carbon monoxide removal plant there should be maintained a desired content of bivalent copper in the wash liquor. The well water at Wesseling was stated to contain only 2-3mg/m³ (surely in error for 2-3mg/litre) of oxygen, which was too little for this purpose, whereas the aerated water was said to contain 10mg/m³ (presumably 10mg/litre). The well water and the aerated wash water were mixed in about equal amounts.

On the other hand, the let-down water at Leuna was used for gas cooling on the conversion plant before being aerated. This was done in order to eliminate oxygen from the converted gas, because the presence of oxygen together with H₂S and H₂O was said to cause corrosion in the gas compressors following the conversion plant (which operated at atmospheric pressure). This Leuna system had been in use for 15 years and there had been no signs of such corrosion. There is no contradiction in these two uses of wash water.

The growth of algæ on the scrubber packing at Wesseling could reduce the throughput of gas to about one-half. It was therefore necessary periodically to shut out a scrubber and to fill it with water which was circulated at 25-30°C while introducing chlorine at two hourly intervals over a period of two days, the amount used every two hours being such that the chlorine content of the water immediately after injection was 100-200mg/litre; this was consumed by the time the next addition was made. Some 50-80kg of chlorine were used in the period of two days, and the treatment disengaged completely the algæ from the packing. They were then removed by draining and flushing the scrubber. At Leuna there was no trouble with algæ, and chlorination was not needed.

As an experiment at Wesseling one scrubber was filled with 80mm rings instead of 60mm. It was stated that the gas throughput could then be increased by 15%, the efficiency of CO₂ removal being unchanged.

Operating data for Wesseling during 1944 are given in Table XXII.

TABLE XXII

OPERATING DATA FOR WESSELING CO ₂ REMOVAL—1944		
Converted gas throughput	120,000m ³ /hr
Average throughput per scrubber	17,000m ³ /hr
CO ₂ in inlet gas	26.8%
CO ₂ in outlet gas	1.8%
CO ₂ removed, calculated from gas	30,000m ³ /hr
CO ₂ recovered on expansion	26,000m ³ /hr
CO ₂ dissolved in expanded water	6,000m ³ /hr
(These figures show some discrepancy)		
H ₂ + CO in recovered CO ₂	7.1%
Water rate in scrubber	4,800m ³ /hr
per 1,000m ³ of converted gas	40m ³ /hr
Proportion of fresh water to aerated water	55 : 45
Temperature of water	8.5-15°C

At Leuna the CO₂ recovered was used partly as an inert gas, partly in the ammonium sulphate plant, while

the rest was blown to waste. No urea was made at Leuna, and only a little solid carbon dioxide for use on the works. No solid CO₂ could be sold because of its objectionable smell, said to be due to organic sulphur compounds formed in the Winkler generators.

b. Removal of Carbon Monoxide

The CO and CO₂ remaining in the gas after the CO₂ scrubbers were washed out under high pressure using an ammoniacal copper solution. The solution was then regenerated by warming at atmospheric pressure and then under vacuum, after which it was cooled and re-used. The gases recovered in the regeneration stage were washed for removal of ammonia, and were then added to the gas entering the conversion plant. The reduction of pressure of the gases evolved from the wash liquor was carried out in an expansion machine so that almost all the energy was recovered for pumping fresh solution to the scrubbers.

The solution used consisted chiefly of cuprous tetrammino carbonate (Cu₂(NH₃)₄CO₃). This compound absorbs one molecule of CO per molecule. The solution, however, contains cuprous copper other than that combined in the complex, but the proportion of cuprous copper present in the complex is increased by maintaining as high a content of ammonia in the liquid as possible, subject to the necessity for keeping the concentration of ammonia below the level at which NH₄HCO₃ crystallises out. When the solution is warmed in the regeneration stage, the CO tends to reduce the cuprous copper to the metal, but this is avoided by the addition of bivalent copper to the solution. Since cupric copper does not absorb CO, it is, however, kept at a low concentration.

The most suitable solution was said to be:—

Specific gravity at 20°C	1.15
Cuprous copper, 1.2gm atoms/litre	= 6.6% by weight
Cupric copper, 0.2gm	= 1.1% " "
NH ₃ , 4.8gm moles/litre	= 7.1% " "
CO ₂ , 2.4gm	= 9.2% " "

It was stated at Wesseling that about two-thirds of the ammonia is combined in the complex, the rest being combined with CO₂.

Theoretically this solution could absorb about 27 times its volume of CO, but in actual operation two-thirds of this capacity was obtained.

In preparing fresh solution, the method formerly used was to pump an aqueous solution of ammonia over metallic copper in the presence of CO₂ and air. Much heat was generated and ammonia was lost. The method recently used was to pump spent solution over metallic copper, when solution proceeded slowly without loss of ammonia.

TABLE XXIII

OPERATING DATA FOR WESSELING CO REMOVAL—1944

Gas rate at inlet	86,000m ³ /hr
Gas rate at outlet	78,000m ³ /hr
Average throughput per scrubber	17,500m ³ /hr
CO content of inlet gas	6.0%
CO content of outlet gas	0.2%
Volume of recovered CO gases	7,000m ³ /hr
Composition of recovered CO gases		21.0% CO ₂
		63.0% CO
		14.0% H ₂
Copper solution washing rate 255m ³ /hr; 3.27m ³ /1,000m ³ of outlet gas		
Washing temperature	20.7°C
Regeneration temperature	39.5°C
Analysis of solution, gm atoms or moles/litre		Cuprous copper 1.20
		Cupric copper 0.22
		NH ₃ 4.90
		CO ₂ 2.50

In operation at Wesseling the only difficulty experienced was the packing of the expansion machine and pressure pump. Chrome-tanned leather was satisfactory, but later it was impossible to obtain. A Buna rubber proved to be a satisfactory substitute.

The throughput of the Wesseling plant was limited by pipe lines of inadequate size, which restricted the liquor rate. Operating results for 1944 are given in Table XXIII.

Cuprous copper	1.2gm atoms/litre
Cupric	0.2gm ..
NH ₃	5.0gm moles/litre
CO ₂	2.5gm ..

The power consumption was stated at Böhlen to be 232kwh/1,000m³ of gas, for both CO₂ and CO removal.

6. PROCESSES OF GENERAL INTEREST TO THE GAS INDUSTRY

i. LURGI HIGH PRESSURE COMPLETE GASIFICATION

The gasification of coal with oxygen and steam under pressure to produce directly a gas suitable either for towns' supply or for synthetic processes was developed by the Lurgi Gesellschaft für Wärmetechnik, Frankfurt-am-Main. The following is a summary of the information concerning the process supplied by the technical staff of the Lurgi Company at Frankfurt, and by engineers of AG Sächsische Werke at Böhlen; for further details reference should be made to a separate subject report (BIOS 521).

The first high pressure gasification plant rated at 3.5 million m³/yr was put to work in 1936 on the AG Sächsische Werke at Hirschfelde (near Zittau) using two generators of 1.15m internal diameter, each capable of producing up to 15,000m³/day. Larger plants with generators of 2.5m diameter were put to work in 1940 on the AG Sächsische Werke at Böhlen (near Leipzig), and in 1942 on the Sudetenländische Treibstoffwerke at Brüx (Czechoslovakia), with capacities of 150 and 80 million m³/yr, or 430,000 and 230,000 m³/day respectively.

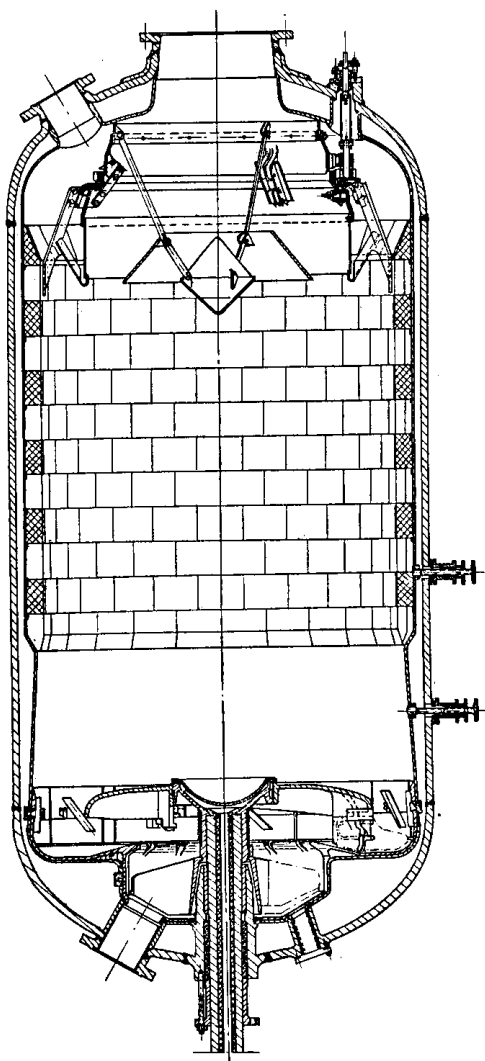
The fuel supplied to these plants is dried brown coal sized 3–10mm with maximum of 20mm. Fuel containing more than 8 to 10% of sizes below 2mm cannot be used. At Böhlen pieces broken off from the corners of brown coal briquettes in handling, prior to low temperature carbonisation, and conforming to the above sizing, were mixed with the brown coal lumps in the proportion of 1:2. Short-period tests have been made with various Silesian hard coals. The gasification pressure employed on these plants is 20ats, and the gas produced is used for towns' supply.

The Böhlen plant is in two parts, consisting of five older generators (1940) and five modern (1943), housed in one building. The modern generators differ from the older type in the design of the charging pouch, grate drive mechanism, and arrangements for scraping the generator dome. Each generator is rated at 3,000m³/hr and is normally operated at 2,500m³/hr. The design calorific value of the gas was 4200k.cal/m³, although war-time difficulties often reduced this to 3,900k.cal/m³. Attempts had been made to raise the calorific value to 4,500k.cal/m³, but this was not possible at the normal working pressure of 20ats; it might be possible at 25ats when methane synthesis would be promoted further.

Oxygen is supplied by a Linde-Fränk plant, consisting of 4 units, two of 1,000m³/hr, and two of 2,000m³/hr oxygen capacity. The oxygen is of about 95% purity and is supplied to the generators at 23ats and 40°C. Steam is supplied from the adjacent power station and is superheated to 500°C by means of waste gas from the charging pouches and pressure water scrubbing plant before entering the generators.

The pressure generator consists of a double-walled spherical-ended cylinder (see Fig. 23), of overall height 6.8m by 3.0m diameter. The cylindrical portion of the generator is brick-lined from the top to within 1m of the grate. The internal diameter is 2.5m and the capacity is 35m³. The annular space between the walls

FIGURE 23



DRAWING OF LURGI GENERATOR

At Wesseling, scrubbing was carried out at 325ats. At Leuna, a similar system was used at 250ats; formate had not been used since 1925; regeneration was carried out at 40°C maximum, using a vacuum in two stages down to 160–200mm Hg absolute.

At the Brabag I plant, Böhlen, there were three towers operating at 300ats. The solution had the composition:—

FIGURE 24

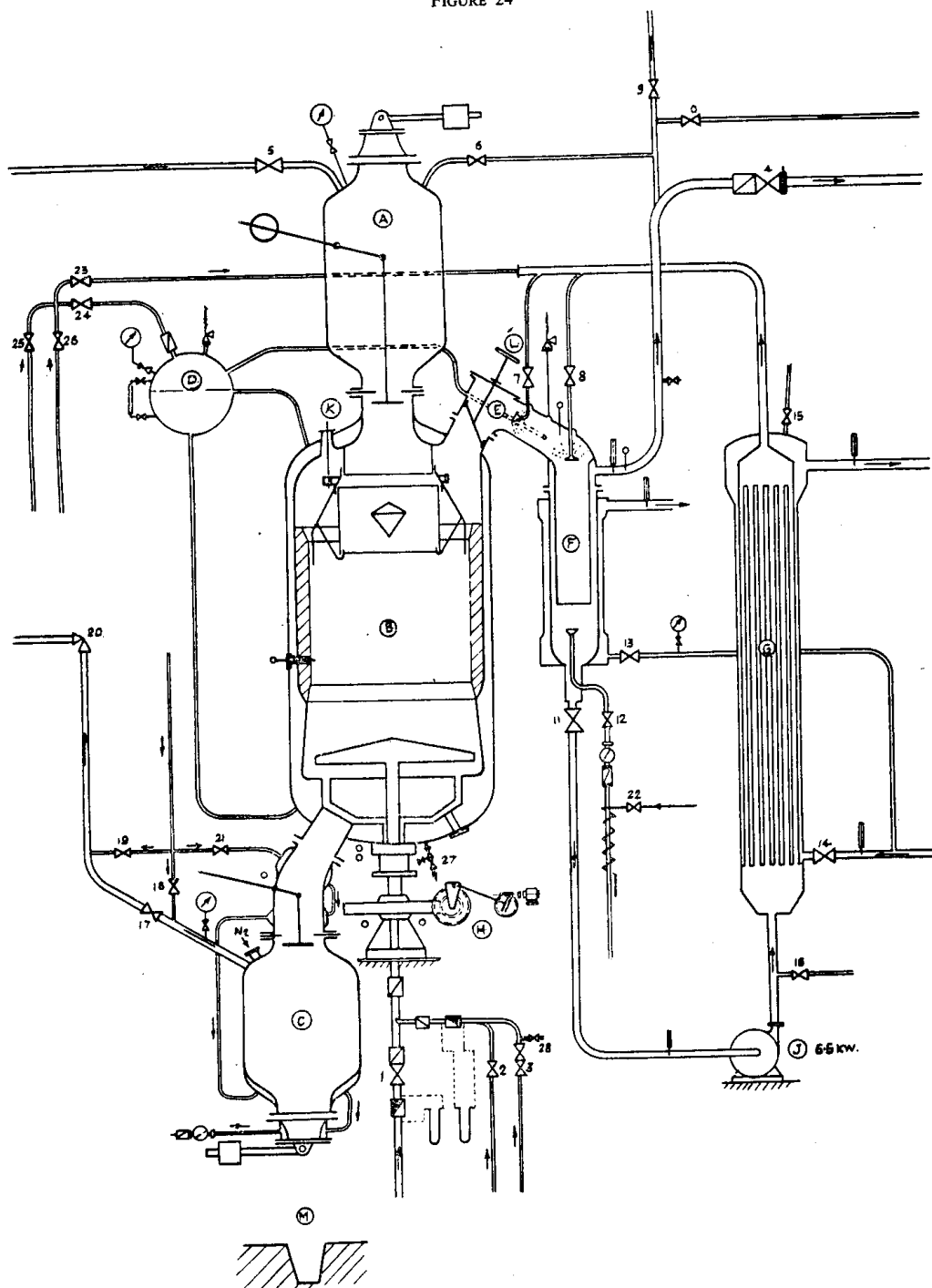


DIAGRAM OF LURGI GENERATOR

forms a water jacket which is connected to a steam drum, the small quantity of steam produced (60kg/hr) being led into the gas offtake. In this way, the pressure inside the water jacket is maintained equal to the pressure inside the generator.

Fuel is charged into and ash is discharged from the generator through pressure pouches. A sketch of a generator equipped with the older type of pouch is attached as Fig. 24. The modern charging pouch consists of a chamber 2.75m high by 2.0m external

diameter, capacity 7.5m³, constructed of M2 boiler steel, and fitted with two cone-type valves. The top valve communicates with the overhead fuel bunker and the bottom valve with the generator. On the Böhlen plant both valves are manually operated, whereas it was stated that on the Brück plant the top valve is operated by means of an hydraulic piston located inside the pouch.

The top valve is composed of H.30.11 steel, and seats against a rubber ring (Buna S) dovetailed into the top flange of the pouch. The normal life of the Buna ring is three months. The bottom valve has a hard ("Panzer") steel removable conical insert which seats against a chrome alloy of 60.11 steel sharp-edged seating, which is usually renewed after one year of service, when the initial line contact has widened up to 7 to 8mm. The free opening of both the top and bottom valves is 250mm diameter.

The method of charging the generator is as follows: The bottom valve is closed and the gas in the pouch blown off to a holder from which it is drawn to burn in a steam superheater; the top valve is opened. As this valve is lowered, it permits a cylinder resting upon it to drop to an extent limited by lugs specifically provided for the purpose, leaving the coal from the bunker free to flow through the cylinder and the space between the bottom edge of the cylinder and the valve into the pouch. When the pouch is full, the top valve is closed. In rising, the valve makes contact with the movable cylinder, thus shutting off the coal, and leaving the contact surface of the valve clean. Gas is then let into the pouch from the generator and finally the bottom valve is opened. It takes five minutes to charge the pouch. The total volume of gas blown off from the coal pouches is 5-7% of the total, and is not included in the reported gas make.

Ventilators are fitted over the coal charging valves to remove any gas escaping and the coal bunkers are purged continuously with nitrogen from the air separation plant.

Gasification is continuous, and the intervals between charging the pouches depend on the relative sizes of the pouch and generator. Actually the interval was 20min with the old generators, and 35-45min with the new generators. A generator can be started up from cold in 12-18 hours if fired with a thin layer of coal on the top of the ash. Air is substituted for oxygen when starting up.

The grate is slightly domed in form, and is composed of three sections in each of which there is fitted a detachable portion which incorporates a plough arranged to direct the ash passing over the edge of the grate into a cylindrical space beneath the grate. A vertical vane attached to the grate shaft then scrapes the ash into an opening leading to the ash pouch. The diameter of the grate is 1.6m, the centre being 150mm above the circumference. The grate sections are preferably cast of 25% chrome steel, and have a normal life of three years. The drive shaft of the grate is hollow to provide the inlet for the oxygen and steam mixture. The grate is driven electrically through reduction gearing and a ratchet device.

The ash leaving the generator passes into the ash pouch through a valve which is exactly similar in construction to the bottom valve of the charging pouch, except that its diameter is 300mm instead of 250mm. The ash pouch is 2.45m high by 1.57m diameter with a capacity of 3.5m³. The base of the pouch is closed by means of a disc clamped by four swing bolts. A thin Klingerite packing ring set into the disc forms the actual joint and this is renewed after every three discharges. The pouch is steam-heated at appropriate points to

prevent condensation of steam on the ash. The ash is discharged through a portable sieve into a water sluice at intervals of about two hours, the oxygen and steam released in the process of reducing the pressure being allowed to escape to atmosphere. Steam is used when building up the pressure again to working level.

The grate is operated continuously, and its speed of rotation is determined by the quantity and character of the ash. The ash zone normally extends 300-500mm above the grate. The temperature of the fuel bed and condition of the ash are controlled by the oxygen : steam ratio. The temperature in the reaction zone was stated to be 1,050 to 1,150°C. The minimum permissible melting point of the ash is 1,100° and fuels containing up to 30% of ash may be used. The carbon content of the ash is from 5 to 6%.

There have been no difficulties with clinker formation except during periods of irregular operation, and the ash discharged is normally very fine. During air raid periods, irregularities in operation led to clinker difficulties necessitating four shut down periods in one year for each generator.

It was stated that a generator can be operated for 250 consecutive days, which, however, include about 30 miscellaneous minor shut down periods totalling 90 hours. Total time lost for both major and minor repairs is of the order of 2,000hrs/yr. Difficulties due to corrosion of parts of the plant by H₂S and oxygen at 20atms have been experienced. Chrome steel containing up to 23% of chromium has proved to be resistant.

The gas leaving the generator at a temperature of about 300°C passes directly to a primary cooler, at the inlet to which it is sprayed with an excess of water. Several experimental designs of primary cooler have been used on the various generators with the object of eliminating troubles due to accumulation of dust. The general design in each case makes use of rapid changes in the direction of gas flow to precipitate tar and any dust. The tar is discharged through a trap and the water is recirculated through an indirect cooler to the sprays. The gas leaving the primary coolers at about 150°C and 20atms is collected separately from each half of the house. Each stream then passes through two vertical water tube coolers, when the temperature is reduced to 100°C. The gas then passes through a tar precipitator of the multi-baffle type and then through three water tube coolers to condense the light oils. It is next washed with oil in a Raschig ring scrubber to recover benzole.

The cooling of the gas and the removal of condensable products is followed by scrubbing under pressure with water to remove CO₂ and H₂S. The total gas is passed through four Raschig-ring packed towers arranged in parallel. The water is recirculated, being first delivered by high pressure pumps to the scrubbing towers and then, after absorbing CO₂ and H₂S, it is expanded to atmospheric pressure through turbines. Gases released from the water in this expansion process are separated and used for steam superheating. The water then flows down four towers, packed with boards on edge, where it is blown with air; this air containing H₂S is then passed to the bottom of the power house chimneys where H₂S and SO₂ were said to react to give sulphur, which is discharged to the atmosphere.

After water washing, the gas passes to the luxmasse purifiers. There are two parallel sets of purifiers; each set consists of four boxes, of which three are used while one is being recharged with oxide. The working life of a charge is about four weeks. The boxes contain five trays, each with two layers of oxide 16-18in deep, the gas flowing in parallel through the 10 layers in a

box, although the three boxes of a stream are worked in series. The gas enters with 10–30gm H₂S/100m³, and leaves with 0.1gm/100m³. It was stated that 20te/yr of luxmasse were used.

The total pressure loss in the whole cooling and purifying plant is 1at, so that the finished gas enters the grid at about 19ats. A flow diagram of the process is given in Fig. 25.

During the visits, several references were made to tests with Silesian hard coal. It appeared quite clearly that these experiments had been conducted for a short period only and that optimum conditions had not been established. On two occasions it was stated that troubles due to sticking and clinking in the generator and to dust blockage in the primary cooler had been experienced during these tests. Reports on these tests were among the documents secured.

In operation, there are three men and one technician per shift in the control room, which contains a panel for each generator, on which are mounted a CO₂ recorder, steam and oxygen flow meters, a pressure recorder, and a five-point temperature indicator. The total number of men assigned to the plant, including those on the Linde oxygen plant, is about 200. This excludes boiler men and power-house attendants.

It was stated that the cost of the gas plant complete with oxygen plant, offices, land and all services totalled RM11,000,000.

The working results for the year 1943 are given in Table XXIV.

TABLE XXIV

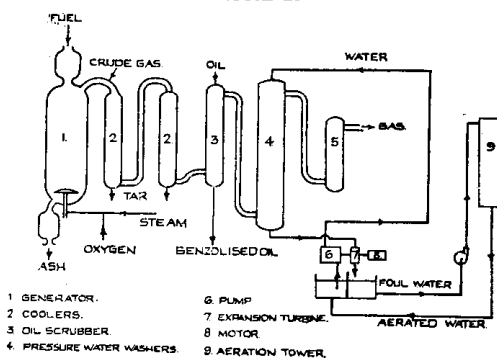
LURGI HIGH PRESSURE COMPLETE GASIFICATION—
OPERATING DATA, 1943

Total volume of purified gas made ..	97,796,608m ³
Gas composition	
CO ₂	7.7%
C _n H _m	0.9%
O ₂	0.2%
CO	18.7%
H ₂	49.6%
CH ₄	22.1%
N ₂	0.8%
Gross calorific value of gas ..	4,360k.cal/m ³
Sp.gr (air = 1) of gas ..	0.486
Tar made ..	11,593te
Benzole made ..	4,483te
Calorific value (gross) of tar ..	9,549k.cal/kg
Sp.gr of tar (60°C) ..	0.933
Calorific value (gross) of benzole ..	9,751k.cal/kg
Sp.gr of benzole (D _{15/15}) ..	0.828
Liquor made ..	108,180m ³
Composition of liquor	
CO ₂	0.485%
NH ₃	0.454%
Phenol	0.499%
Tar	1.125%
Tar content of liquor ..	11.25gm/litre (1.125% by weight)
Maximum daily gas production ..	401,982m ³
Mean daily gas production ..	267,936m ³
Mean hourly generator output ..	2,495m ³
Mean hourly generator loading of dried coal ..	0.794te/m ³
Total quantity of coal gasified ..	
As delivered ..	156,244te
Amf basis ..	106,319te
Calculated composition of mixed coal	
Combustible material ..	68.1%
Water ..	21.0%
Ash ..	10.9%
Tar content ..	13.6%
Carbonisation water ..	26.9%
C (amf) ..	69.49%
H ..	5.85%
S ..	3.08%
N + O ..	21.57%
Gross calorific value ..	7,014k.cal/kg
Gas yield based on coal as delivered ..	628m ³ /te
„ „ amf basis ..	920m ³ /te

TABLE XXIV—continued

Tar and benzole yield based on content in coal				75.8%
Tar loss in gas liquor				5.8%
Thermal efficiency calculated from gross calorific value:				
<u>Gas + tar + benzole</u>		=	78.0%	<u>Gas</u>
Coal				Coal = 57.2%
Quantity of released gas				42,780,295m ³
Composition of released gas				
gas				CO ₂ .. 84.5%
				H ₂ S .. 3.9%
				C _n H _m .. 0.5%
				O ₂ .. 0.2%
				CO .. 2.2%
				H ₂ .. 4.6%
				CH ₄ .. 3.3%
				N ₂ .. 0.8%
Gross calculated calorific value of released gas				860k.cal/m ³
Purity of oxygen				95.0%
				<i>Actual</i> .. <i>Per m³ of purified gas</i>
Pure oxygen				14,083,721m ³ .. 0.144m ³
Steam for gasification				127,022te .. 1.30kg/m ³
Total steam				154,425te .. 1.58kg/m ³
Electricity				25,010,256kwh .. 0.256kwh/m ³
Plant water				2,056,452m ³ .. 21.0 litres/m ³
Recycled cooling water				353,868m ³ .. 3.6 litres/m ³
Staff employed				15
Workmen employed				173
Total man-shifts				50,259
Gas produced per man-shift				1,942m ³

FIGURE 25



FLOW DIAGRAM OF PRESSURE GASIFICATION PLANT

The total power consumption for oxygen production, including compression to 23ats, is 1.205kwh/m³, and the cost 2.2pfg/m³, including capital charges. The power for oxygen production, excluding compression, 0.9–1.0kwh/m³, is high because the turbo-compressors on the plant are inefficient. It was hoped, by fitting new rotors, to reduce the power consumption for uncompressed oxygen to 0.8kwh/m³.

Based on costs of fuel at RM6.50/te, water at 6pfg/m³, power at 1.1pfg/kwh, labour at 0.4pfg/m³ of gas, maintenance cost at 0.4pfg/m³ of gas, and oxygen at 2.2pfg/m³, the total cost of gas is 3.8pfg/m³. After deducting a by-product credit of 1.4pfg/m³, the nett cost is 2.4pfg/m³.

The engineers in charge at Böhlen stated that the gasification plant operated smoothly and satisfactorily and was a most successful unit.

The documents secured appear to cover the more important structural details of the gasification plant, and include instructions to employees on the methods of operation, and daily and monthly reports of operation for several years from starting up.

ii. METHANISATION

A process for increasing the methane content of coke oven gas by conversion of carbon monoxide and dioxide was carried out at Sterkrade Holten by Ruhrchemie AG. The catalyst was nickel, magnesium oxide and kieselguhr in the ratio of 100 : 10 : 50.

For the preparation of the catalyst, 24 litres of a solution of nitrate containing 42gm/litre nickel and 6.2gm/litre magnesium oxide and 40 litres of a solution of sodium carbonate containing 80gm/litre, were heated to boiling and the nitrate added to the soda solution with stirring. After precipitation was complete, 0.5kg kieselguhr was added and well mixed by stirring. The catalyst was then filtered off in a press and washed with 220 litres hot water and the moist cake extruded on to a belt heated by an open flame. Some magnesia is lost during the washing process. The product was then broken to 3-5mm in a special mill and reduced for one hour at 350°C with a 3 : 1 H_2/N_2 mixture at a space velocity of 6,000-8,000/hr, and cooled to below 100°C in the same gas. It was then saturated with carbon dioxide.

In the process, coke oven gas from which the organic sulphur compounds had been removed passed over the catalyst at 160-215°C; as low a temperature as possible was used, control being to within 1-2°C. Increase in temperature was made only to compensate for decreasing catalyst activity. The catalyst was contained in the 28mm diameter tubes of a multi tubular vessel. Steam generation in the shell provided good temperature control.

iii. SEPARATION OF ETHYLENE AND METHANE FROM COKE OVEN GAS

A plant designed by Still for the extraction of ethylene

and methane from the coke oven gas at Nordstern was in course of erection, and was very nearly complete when the works was put out of action by bombing in February, 1945. The process was new and was in the nature of an experiment.

1,700,000m³/day of purified gas were to be cooled to 4°C and scrubbed with sulphur-free benzole at 8ats. The rate of benzole circulation was to be 500m³/hr. The rich benzole was to be distilled, and the vapours compressed to 42ats before fractionation into ethylene, methane and other hydrocarbons. The cooling was to be effected by an ammonia refrigeration plant.

It was intended to send the ethylene to Hüls for rubber synthesis, while the methane and higher molecular weight hydrocarbon gases were to be compressed into cylinders for any suitable purpose.

The estimated daily yields were as follows:—

Ethylene	24te
Methane	28te
Other hydrocarbons	7½te

The estimated consumptions were:—

Steam	26te/hr
Electricity	2,060kw/hr
Water	845m ³ /hr
Recirculated water	735m ³ /hr

Documents found at the offices of the Lurgi Gesellschaft für Wärmetechnik, Frankfurt-am-Main, showed that this Company had also made an intensive laboratory study of this problem. Their conclusion was that up to 10ats operating pressure, it is preferable to absorb ethylene and methane with active carbon, preferably nut-shell charcoal, at a reduced temperature. When operating at higher pressures, a preliminary concentration by oil washing, e.g. with benzole, was preferred.

C—Hydrogenation Processes

1. INTRODUCTION

In this report, the term "hydrogenation" is taken to cover all the activities of the German factories which were classified as "Hydrierwerke" for the purpose of control and co-ordination of liquid fuel production.

The chief activity at most of these factories was production of aviation and motor petrol from indigenous raw material such as coal and coal tar, using the process of destructive hydrogenation. During the war, the necessity to produce maximum quantities of high quality special aviation fuels resulted in the erection of plant for "hydroforming" both hydrogenation and natural petroleum petrol products, and for the synthesis of branched paraffin aviation fuel components such as iso-octane and alkylate. Usually these plants were built as auxiliaries to destructive hydrogenation factories, and used hydrogenation products as their raw material. Exceptions were Moosbierbaum, which operated only the hydroforming process, and Heydebreck and Auschwitz, whose contribution to fuel production was limited to synthesis of iso-octane from isobutyl alcohol.

The interdependence of destructive hydrogenation, hydroforming and branched paraffin synthesis processes in the German oil production programme is shown in the attached chart (Fig. 26), and these three groups of processes, as operated in Germany, are described in detail in the separate sections which follow.

2. EXTENT OF GERMAN HYDROGENATION ACTIVITIES

At the outbreak of war, Germany already had seven destructive hydrogenation plants in operation, six of which were working substantially to the full capacity of the installed equipment while the seventh was just starting up. The total installed capacity of these plants was about 1,400,000te/yr of oil plus liquefied gas products, and the actual production rate in the latter part of 1939 was about 1,150,000te/yr.

Table XXV lists the plants operating before the war, and shows the raw materials employed and the individual plant outputs.

At the beginning of the war, none of the plants was equipped for secondary processes such as hydroforming of petrol naphtha or synthesis of octane or alkylate from by-product butane.

The erection of three additional destructive hydrogenation plants at Stettin-Pölitz, Lützkendorf and Wesseling had been started before the war. The first two came into production in mid 1940, and Wesseling started up at the end of 1941. Later, two large factories were erected at Briix and Blechhammer, and these first came on to line in late 1942 and early 1944 respectively. All the older hydrogenation plants were greatly extended during the war, and in many cases auxiliary plant for