I. INTRODUCTION

The Ludwigshafen and Oppau plants are largely independent I. G. factories situated some 2 - 3 miles apart on the west bank of the Rhine facing Mannheim. The former factory is a general organic chemical works specializing in dyes, dye intermediates, plastics and synthetic rubber, while the latter is a heavy organic chemical factory producing ammonia, methanol, higher alcohols and their derivatives. Before the war much of the I. G. research and development work was carried out at Ludwigs-hafen; in particular the high pressure research section directed by Dr. Mathias Pier played a very active part in all hydrogenation developments.

Apart from the possibility that a full scale hydrogenation or Fischer Tropsch plant had been erected at Ludwigshafen/Oppau during the war, the main objectives of an oil team investigation were: -

(a) To obtain from Dr. Pier and his staff an advance general picture of German fuel production processes.

(b) To study the fuel developments still in the research and pilot plant stage.

(c) To examine any new developments in hydrogen or synthesis gas manufacture.

(d) To look for new processes for production of high anti-knock fuel constituents and for new fuel additives.

(e) To investigate new chemical syntheses based on raw materials obtainable from oil.

The Ludwigshafen and Oppau factories were first visited by the large team listed in Appendix A during the period 25-31st March. The investigation revealed that no large plant for synthetic fuels or lubricants had been operated at this target. All the important members of the Fuel Research Section staff had been evacuated to Heidelberg and information on the work of this department was therefore limited to that contained in seized documents, the greater part of which have still to be examined in detail. Valuable information on synthesis gas production from hydrocarbon gases was obtained as well as interesting data on a number of chemical syntheses.

Two members of the above team - Holroyd and Faragher - accompanied by Major Tilley (interrogator) went on to Heidelberg, contacted Dr. Pier and the chief members of his staff on April 1st and obtained from them the hydrogenation information given later in the body of the report.

Later, after visiting Leuna, Holroyd, Faragher and Ellis paid a second visit to Heidelberg and to Ludwigshafen/Oppau on 27th-30th May to check a number of details, particularly with respect to hydrogenation costs, and to obtain information on the pressure conversion of water gas to hydrogen and on the manufacture of Wickel pressure vessels.

The following report presents, under subject headings, the information obtained in the course of these various visits.

II. SYNTHESIS GAS PRODUCTION

(A) General

Oppau had a maximum capacity for production of 180,000 M^3/hour of synthesis gas plus 40-50,000 M^3/hour of producer gas. Synthesis gas was made mainly from water gas produced from coke in 31 generators of conventional design, the novel feature being that three of the water gas to hydrogen shift units operated a 25-30 ats. pressure process.

The remaining synthesis gas was obtained by Linde fractionation of Saar and Ruhr coke oven gas to give hydrogen, and by a modified methane-steam process (the Methane-Oxygen or K.W. process) from coke oven gas or hydrocarbons recovered by Linde fractionation of coke oven gas. The latter process was operated in two large scale pilot units at Oppau and these had a total capacity of 20,000 M^3/hour synthesis gas. The units had also been run experimentally using a modified process which gives rise to acetylene as a by-product.

Both the pressure shift and the methane-oxygen processes are of particular interest because they have been adopted extensively in the new eastern plants built during the war. They were therefore investigated in considerable detail and are described fully in the following sections.

(B) Pressure Operation of the Water Gas "shift" reaction.
(i) Objectives behind the Development.

Information on this process was obtained from Dr. Schieranbeck, Ing. Lampe, Ing. Funk during the second visit to Oppau. Dr. Schieranbeck had directed the I. G. development work in this field and Ing. Funk had been in charge of a large scale installation at Blechhammer.

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 $CO + H_2O = CO_2 + H_2$ 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, the equilibrium of the reaction is unaffected by pressure. Pressure operation therefore simply increases the volume of gas (measured at NTP) which can be treated in a plant of given size and catalyst capacity. No change in reaction temperature and no special catalyst is necessary. The I.G. use a catalyst consisting of 91% Fe_2O_3 and 7% chrome oxide for both pressure and atmospheric units.

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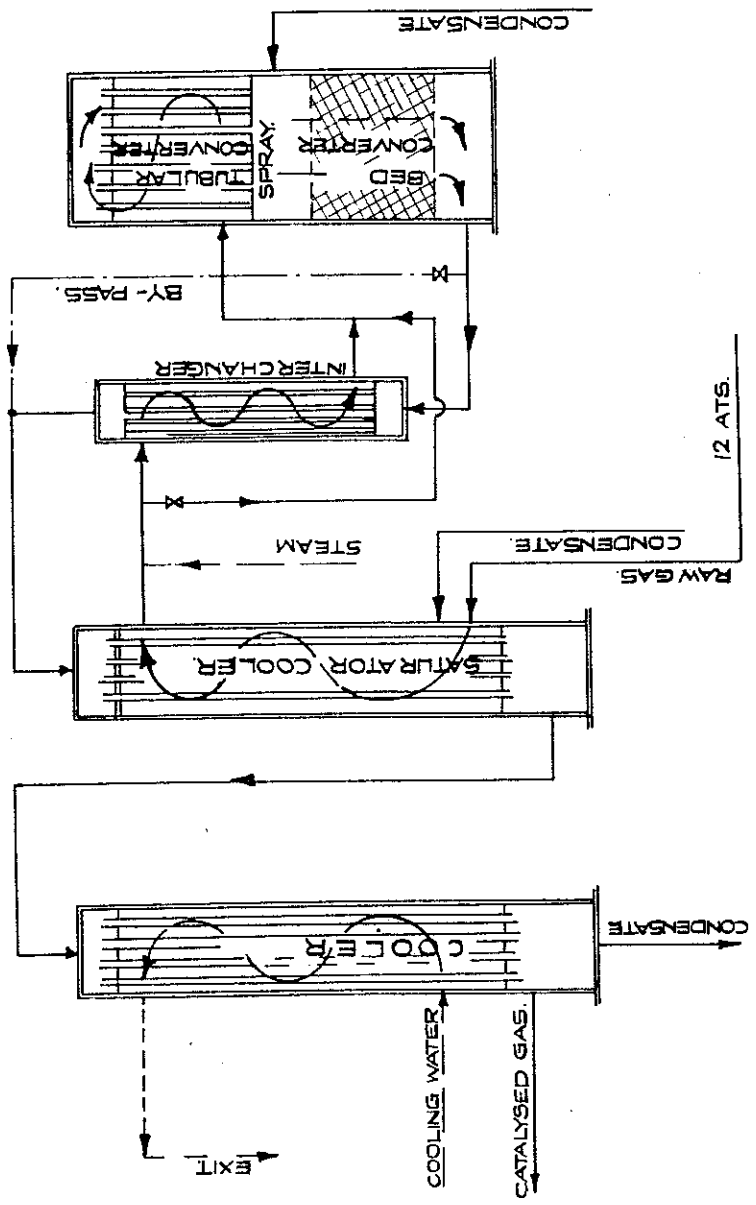catalyst
7%

SCHIERENBECK - SYSTEM - BLECHHAMMER O.H.W.

FIG. I

LOW PRESSURE CO CONVERSION - LEUNA.

COOLING WATER - APPROX. 5 ℓ/m³

CAT. GAS.

15°

25°

CO₂	CO	H₂	N₂
32·8	3·0	-	-

50°

COOLER

70

80°

380°

100g/m³ CONDENSATE.

INTERCHANGER

| I 550° | II 420° 450° |

170°

78°

420g STEAM/m³ RAW GAS.

SATURATOR

65°

100°

25°

CO₂	10·0
CO	38·0
H₂	37·0
N₂	15·0

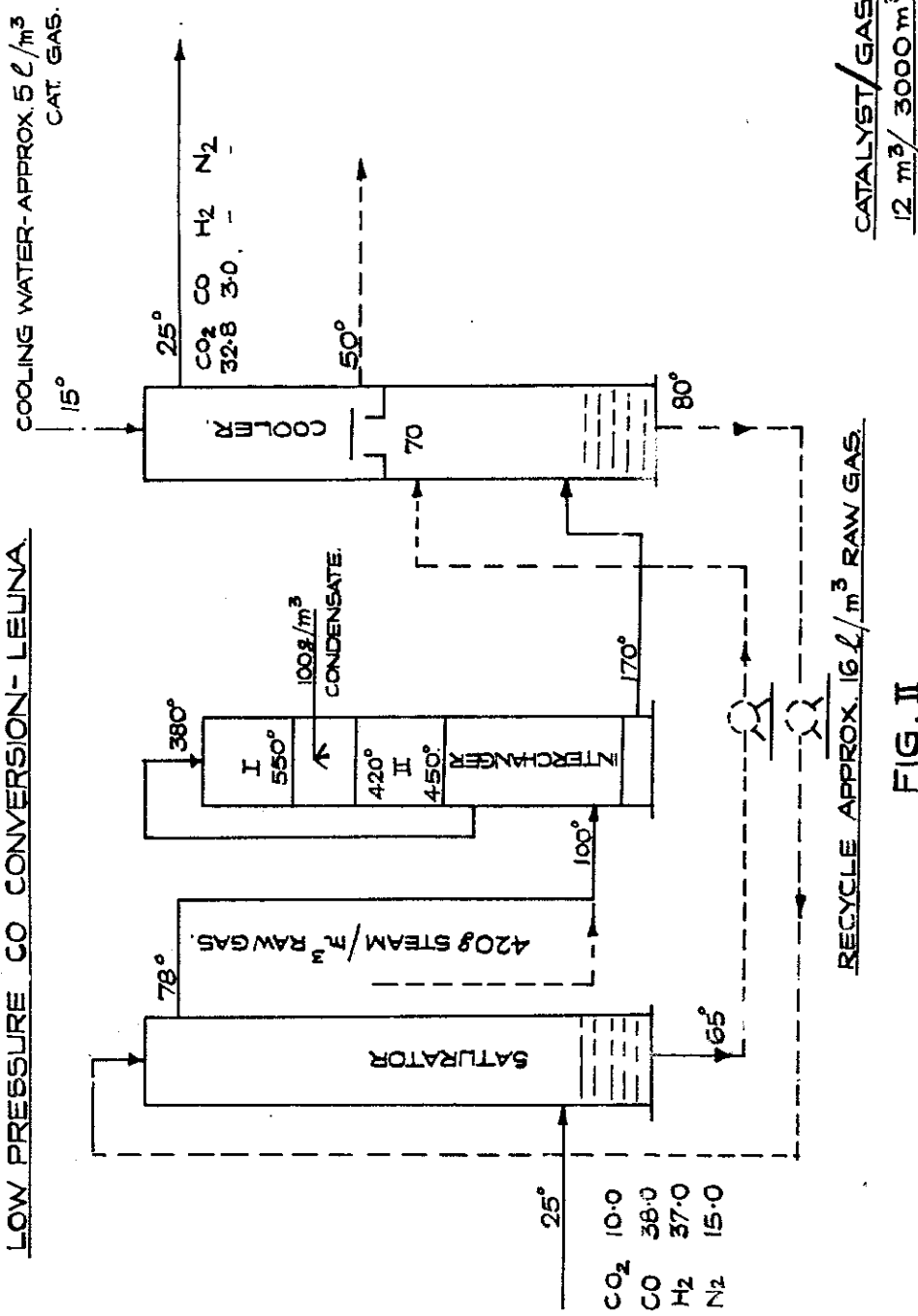RECYCLE APPROX. 16 ℓ/m³ RAW GAS.

CATALYST/GAS
12 m³/3000 m³

FIG. II

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 economy in steam. Under normal atmospheric pressure conditions one of the chief heat losses from the system 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 figure II. 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.

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.

(ii) Description of Plant

The pressure plant developed by the I.G. attempts to secure all three of the above advantages. A flow diagram of the plant is shown in figure I and, for comparison, figure II illustrates a typical low pressure unit.

The feed gas under a pressure of 12-30 atmospheres together with condensate water is introduced to the shell of a tube interchanger (40 mm 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 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 I.G. design for this saturator/heater employs flattened tubes of 4 mm/60 mm 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 4 mm.

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 ingoing 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 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 figure III. 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 figure III 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. The I.G. at Oppau prefer to use 17% chrome steel, but have used V_2A and occasionally FF_6N 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	I.G. Design	25 ats.
Blechhammer	" "	12.5 ats.
Heydebreck	" "	30 ats.
Auschwitz	" "	21 ats.
Brux	Bamag "	12.5 ats.
Linz	I.G. "	30 ats.
Lutzkendorf	Bamag "	8 ats.

(iii) Comparison of the Pressure and Atmospheric Processes.

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

It is unlikely that this increase in unit capacity results in any appreciable reduction in capital cost per M^3 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 100,000 M^3/hour synthesis gas, give pressure units with a total capacity of 125,000 M^3/hour would have to be installed compared with say 11 atmospheric units with a total capacity of 110,000 M^3/hour.

On the operating side there should be a saving in labour and repairs, but the former will be small because labour requirements for any
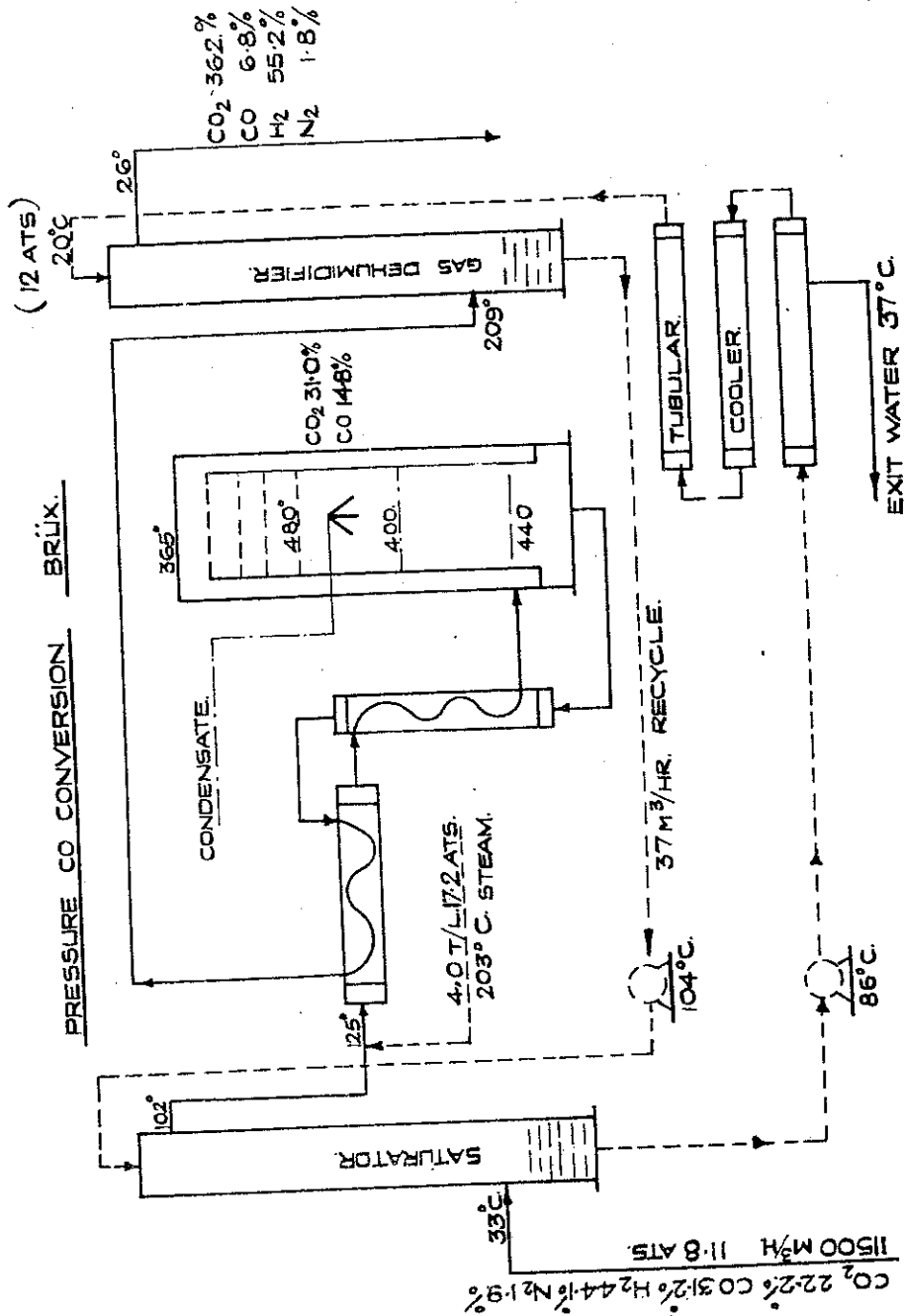
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PRESSURE CO CONVERSION. BRÜX.

CO₂ 22.2% CO 31.2% H₂ 44.1% N₂ 1.9%

1500 M³/H   11.8 ATS

SATURATOR

33°

102°

125°

4.0 T/L 17.2 ATS.
203°C. STEAM.

CONDENSATE.

365°

480°

400.

440

CO₂ 31.0%
CO 14.8%

209°

GAS DEHUMIDIFIER

(12 ATS)
20°C

26°

26°

CO₂ 36.2%
CO 6.8%
H₂ 55.2%
N₂ 1.8%

37 M³/HR. RECYCLE.

104°C.

86°C.

TUBULAR

COOLER

EXIT WATER 37°C.

FIG. III

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 25-30 ats. process is only 250 grams per M^3 of inlet gas compared with 400 grams for the atmospheric pressure process. The I.G. seem to set great store by this 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 H.P. 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 Fischer Tropsch is being made.

The I.G. 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 management of the new plants in Eastern Germany, on the other hand, are dissatisfied with the process and the Brux 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 30 atmospheres, and it was only in the late manufacturing stages that it was realized that the plant was to operate at $12\frac{1}{2}$ atmospheres. 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.

(c) The Methane-Oxygen Process for Synthesis Gas Production.

(i) General Process Description

The following information was obtained (a) by interrogation of of Dr. Kosbahn (assistant to Dr. Sachsse who was mainly responsible for the development of the process) and (b) Dr. Sachsse's Oppau office.

The process provides an autothermic method for the production of synthesis gas ($CO + H_2$ or $CO + H_2 + N_2$) from gaseous hydrocarbons. The first step consists of burning the preheated hydrocarbon ($650°C$) with oxygen or oxygen-enriched air, the amount of oxygen used being substantially the theoretical requirement for the reaction $CH_4 + \frac{1}{2} O_2 = CO + 2 H_2$.

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Actually the reactions occuring in the burning zone are considerably more complex; some CH_4 is burnt completely to CO and H_2O while some remains unchanged. Mainly as a result of the above side reactions, the temperature of the gases is the burning zone is raised to at least $1200^{\circ}C$. The products from this stage thus have sufficient sensible heat for the next step of the process, which consists of the conversion of residual methane by the methane-steam reaction and the attainment of the water gas equilibrium. These secondary reactions are brought about by passing the reactant gases through a bed of nickel-on-magnesite catalyst. The final product leaves this catalyst bed at $800-900^{\circ}C$ 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

$$CH_4 + \tfrac{1}{2} O_2 = CO + 2 H_2$$
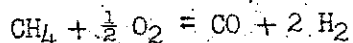
Heat of reaction at $650^{\circ}C = +269 \ WE/M^3$ of CH_4

(2)   2% of methane feed reacting according to the reaction

$$CH_4 + H_2O = CO + 3 H_2$$
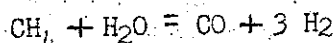
Heat of reaction at $650^{\circ}C = -2689 \ WE/M^3$ of CH_4

(3)   The reaction $CO + H_2O \quad CO_2 + H_2$ 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 .2%. The consumptions per M^3 of CH_4 fed are oxygen .487 M^3, steam .107 kg., cooling water at $15^{\circ}C$. 9.6 kg. The above figures are taken from the preliminary design data for a plant to be erected at Heydebreck which are given in more detail in Appendix B (2).

The process requires a hydrocarbon feed which is very low in sulphur. It was stated that the presence of 15 mg of sulphur/M^3 of methane feed necessitates an increase in reaction temperature of about $200^{\circ}C$.

It is unnecessary to use pure hydrocarbons as feed. Coke oven gas or purge gas from methanol synthesis is also suitable. It is also possible to work with oxygen-enriched air instead of pure oxygen when ammonia synthesis gas is the required product. No satisfactory flowsheet figures are available, however, on these applications. It would appear from the data for pure methane given above that, unless much improved heat exchange efficiency is obtained, considerably more oxygen than corresponds to reaction (1) above would be required. It is hoped that further information will be forthcoming either from a closer examination of documents or from further contacts with the I.G. staff.

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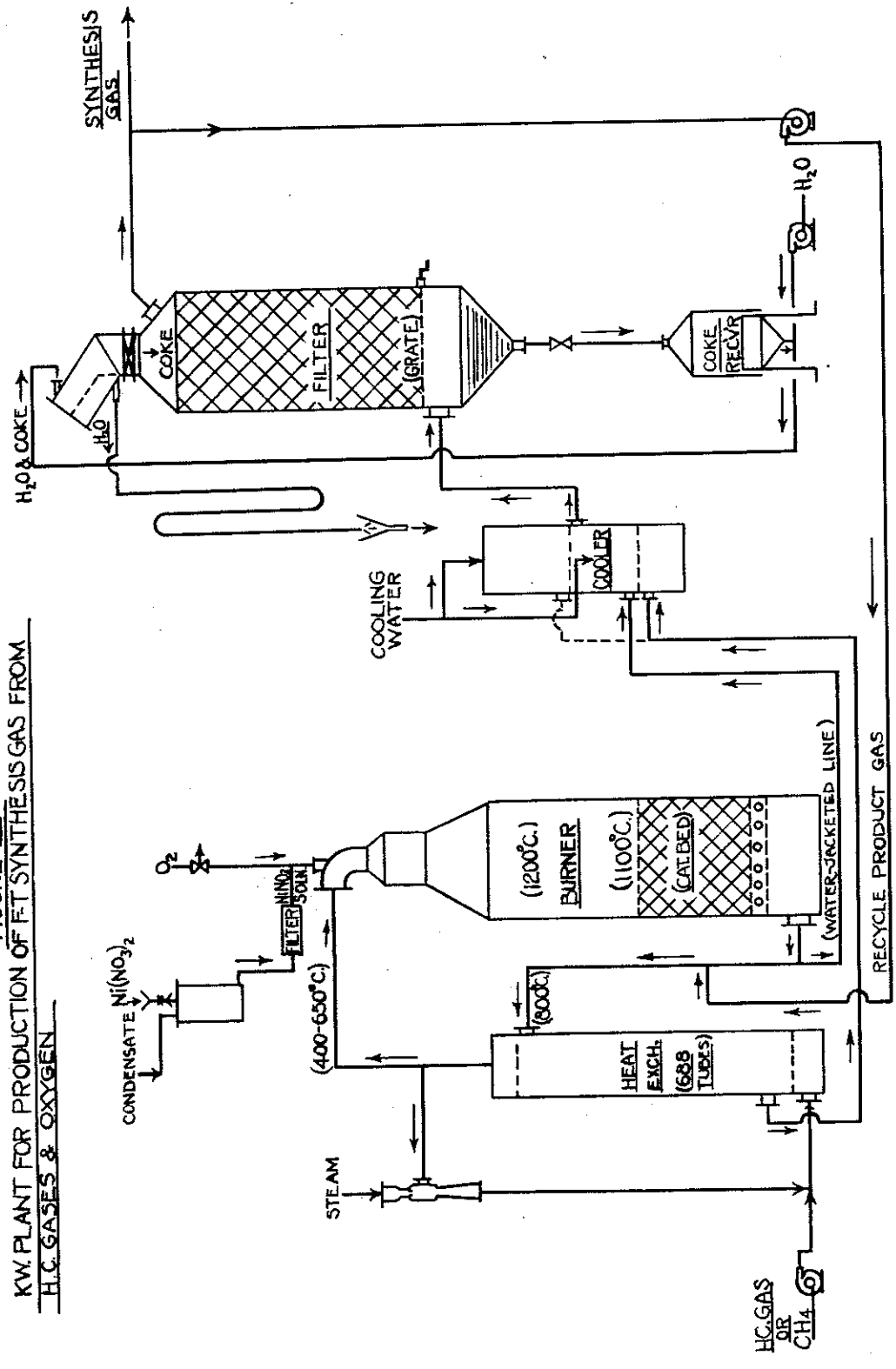pro-
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FIGURE V
KW. PLANT FOR PRODUCTION OF FT SYNTHESIS GAS FROM
H.C. GASES & OXYGEN

SYNTHESIS GAS

H_2O

COKE — FILTER — (GRATE)

COKE RECVR

H_2O COKE

H_2O

COOLER

COOLING WATER

CONDENSATE $Ni(NO_3)_2$

FILTER — $Ni(NO_3)$ SOLN

O_2

BURNER (1200°C.) (1100°C.) (CAT BED)

(WATER-JACKETED LINE)

RECYCLE PRODUCT GAS

(400-650°C.)

HEAT EXCH. (688 TUBES)

(800°C.)

STEAM

H.C. GAS OR CH_4

(SCHEMA BL 4)

FIGURE V.

KW PLANT   MIXING ZONE.
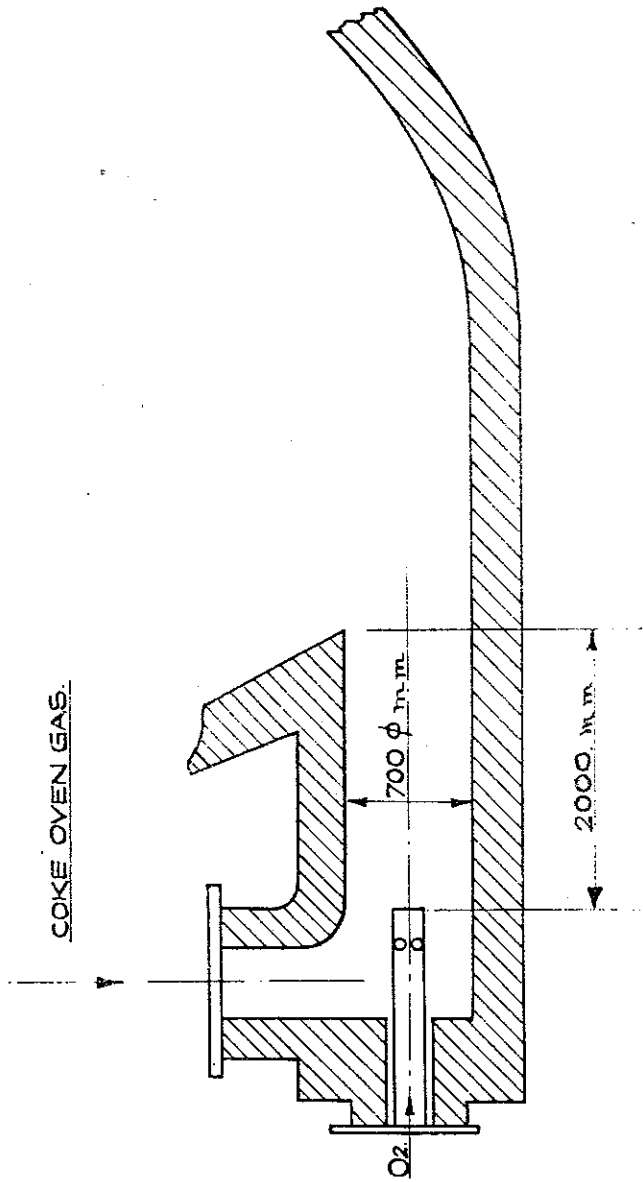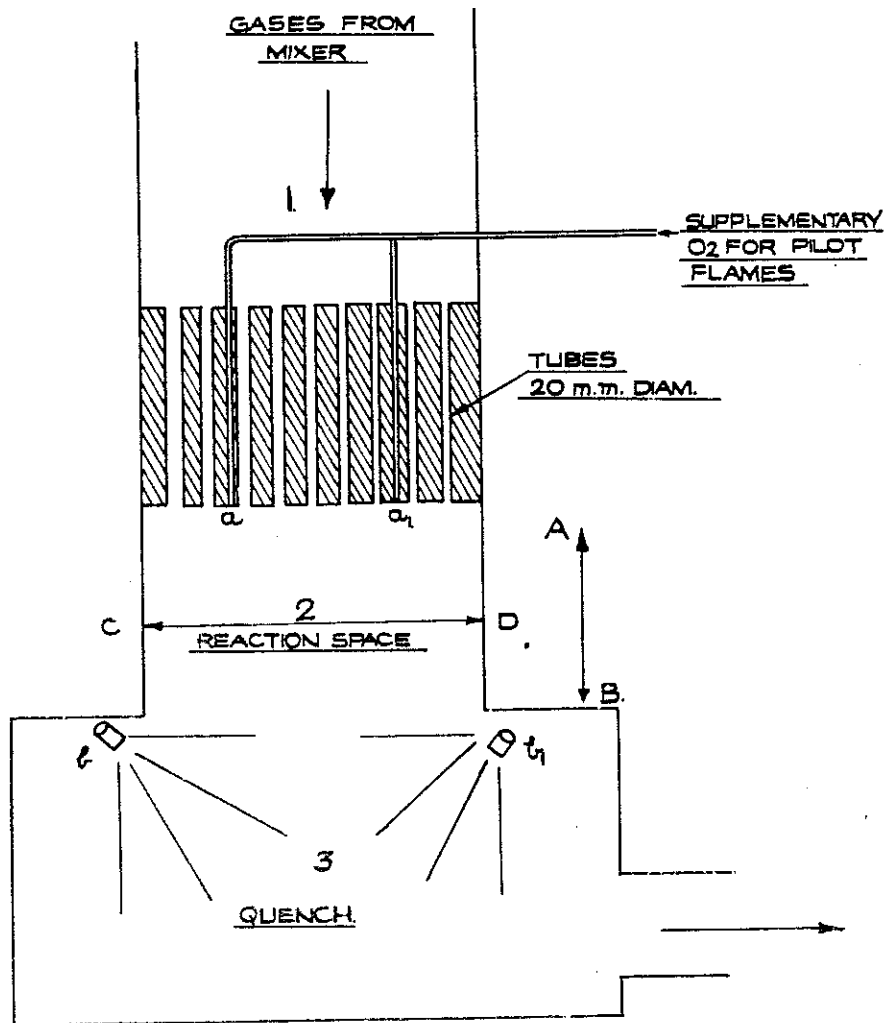
COKE OVEN GAS.

700 φ m.m.

2000. m.m.

O₂.

FIGURE VI.

K.W. PLANT – ACETYLENE BURNER (SCHEMATIC)

REACTION SPACE. CROSS SECTION CD IS $2 \times$ HEIGHT AB TO PREVENT
CARBON DEPOSIT. a & a_1 ARE O_2 LEADS TO MAINTAIN
A CONSTANT FLAME TO START REACTION.

b & b_1 WATER JETS TO QUENCH REACTION.

IF AB IS LONGER CARBON BLACK IS FORMED AND
C_2H_2 7-8%. IF OVERCOME WITH HIGHER THROPUT
THE FLAME BECOMES UNSTEADY

OUTLETS FROM 1 TO 2 NOT OVER 20 m.m.