It is interesting to note that the methane-oxygen process has been adopted at Heydebreck, Waldenburg, Auschwitz and Linz in preference to the methane-steam process, and when rather fuller data are available, it will be of considerable interest to compare these two methods. Using pure methane, the methane-oxygen process gives little more than 75% of the yield of synthesis gas which can be obtained by the methane-steam method and requires substantialquantities of oxygen. On the other hand, no external fuel gas is required and the use of a tube reactor is avoided. The methane-oxygen process also has the advantage that it produces directly a high CO content gas suitable for synthesis of methanol, higher alcohol or Fischer Tropsch product.

(ii) Plant Operation and Details of Equipment

The following description relates to a plant treating 6-7,000 M^3/hr of coke oven gas. A line diagram of the process is shown in Fig. IV.

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. Further details of the Oppau and Heydebreck heat exchangers are given in Appendix B (1). 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. V. This 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 .25 - .30 ats tangentially to the stream of oxygen which enters through a vertical central tube at a pressure of .5 - .6 ats. 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 20 mm. tubes in which the gas velocity is greater than the critical extinction velocity of the reaction, see Fi . VI.

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. This arrangement is shown in Fig. VI. The burner section of the reactor, which

is 11½ ft. external diameter, is lined with 15" of refractory material in order to withstand the temperature of 1200-1500° C which is reached in this stage.

The products of the combustion zone pass downwards through a catalyst bed approximately 6 ft. deep and 9 ft. 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 40 ft.

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. is cooled in spray coolers. Facilities are provided for passing a part of the exit gas from the reactor direct to the coolers as a means of control on the preheat of the hydrocarbon feed. Further control is provided by recycling, if necessary, a small quantity of cooled and clean synthesis gas to the interchanger.

Gas from the cooler finally passes through filter beds of ¼" coke for removal of soot and tarry residues. These filters are cylindrical shells about 20 ft. high and 12 ft. diameter with conical ends. The bed of coke is supported on a movable grate situated just above the bottom cone. The grate is manipulated to permit a slow discharge of coke. Discharged coke falls through a column of water maintained in the bottom cone and this washes off the deposited soot. The clean coke is returned to the top of the filter by means of a water lift, the water is removed by a screen and the coke admitted intermittently to the filter through a slide valve. The rate of coke recycle corresponds to a coke travel through the filter of about 3"/minute.

(iii) Costs

No German cost data were obtained. In view of the interest in comparing this process with the methane-steam method, a special effort should be made to acquire fuller details of utilities consumption and labour requirements as well as more complete general technical information on the application of the process to a feed such as coke oven gas.

(D) Methane-Oxygen Process for Production of Acetylene and Synthesis Gas

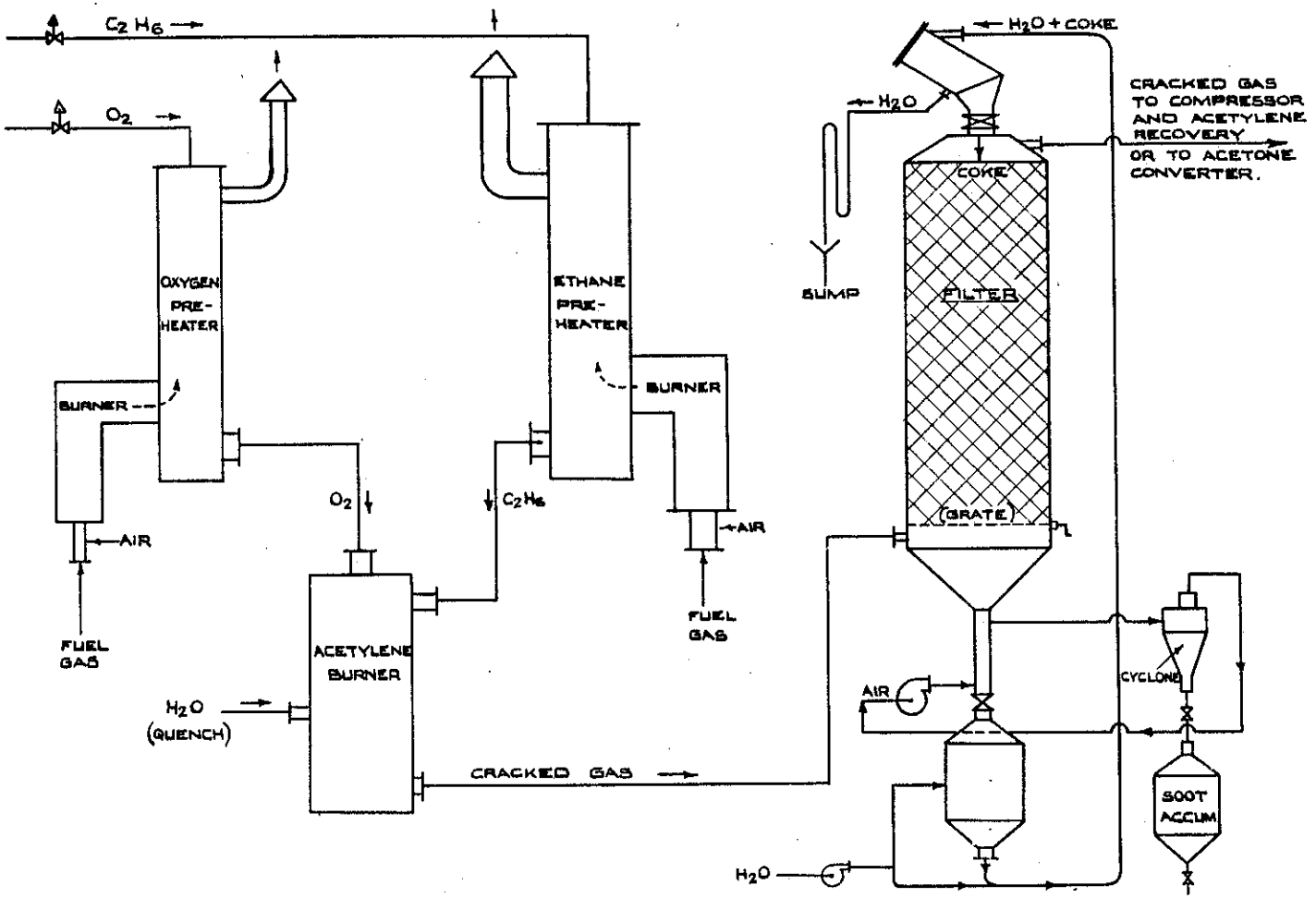
(i) Process Details

Substantially 100% hydrocarbon gas and pure oxygen are necessary for this process. It consists essentially of the burning stage of the normal synthesis 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. VIII. Both the hydrocarbon gas and the oxygen have to be preheated to 400°C in gas-fired

FIGURE VII

KW PLANT FOR PRODUCTION OF ACETYLENE FROM ETHANE AND OXYGEN



REF. SCHEMA BI-1

FIGURE VIII

KW PLANT - ACETYLENE BURNER (DETAIL)

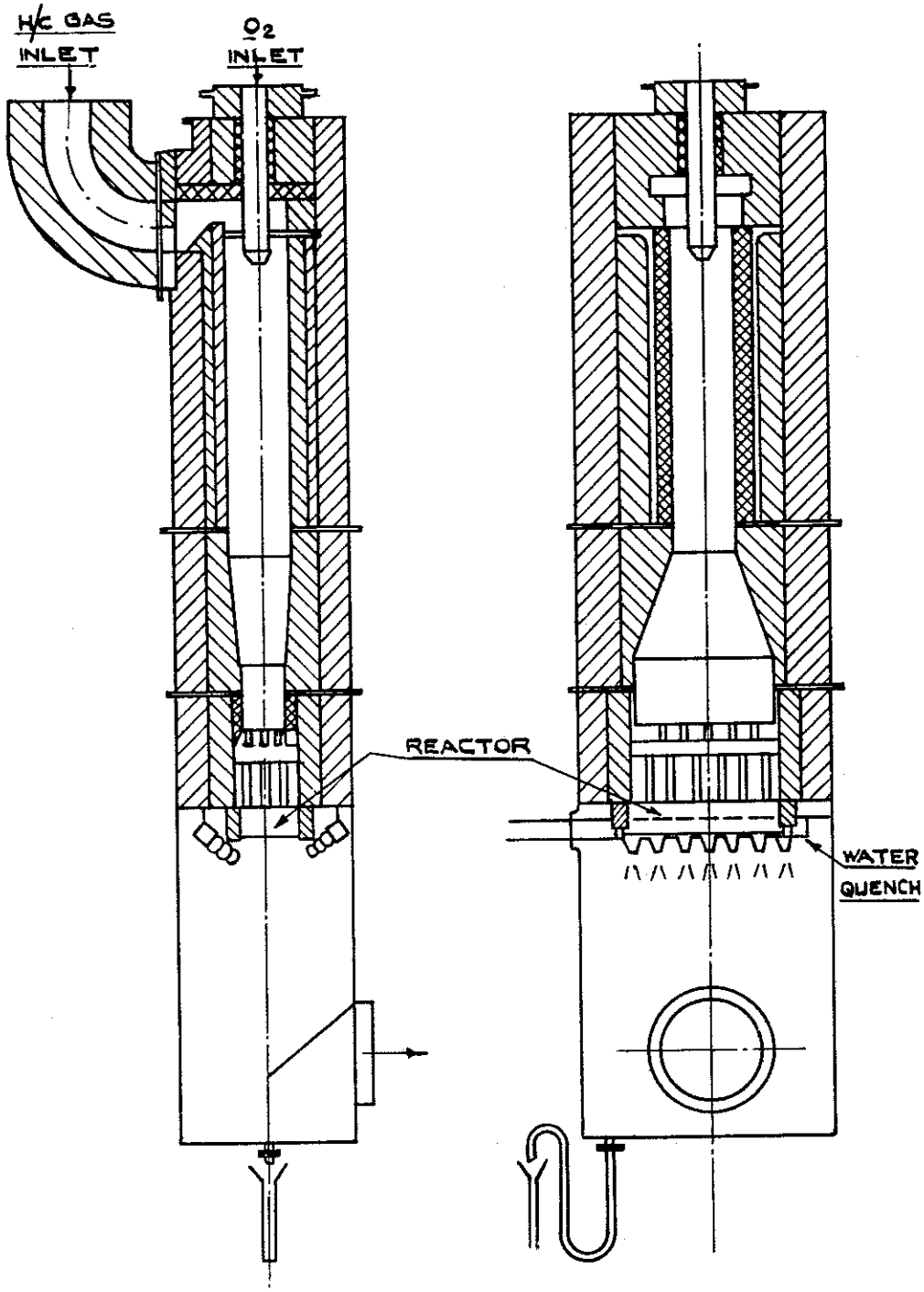


FIGURE IX

PROPOSED FLOW PLAN OF HEYDEBRECK ACETYLENE OPERATION

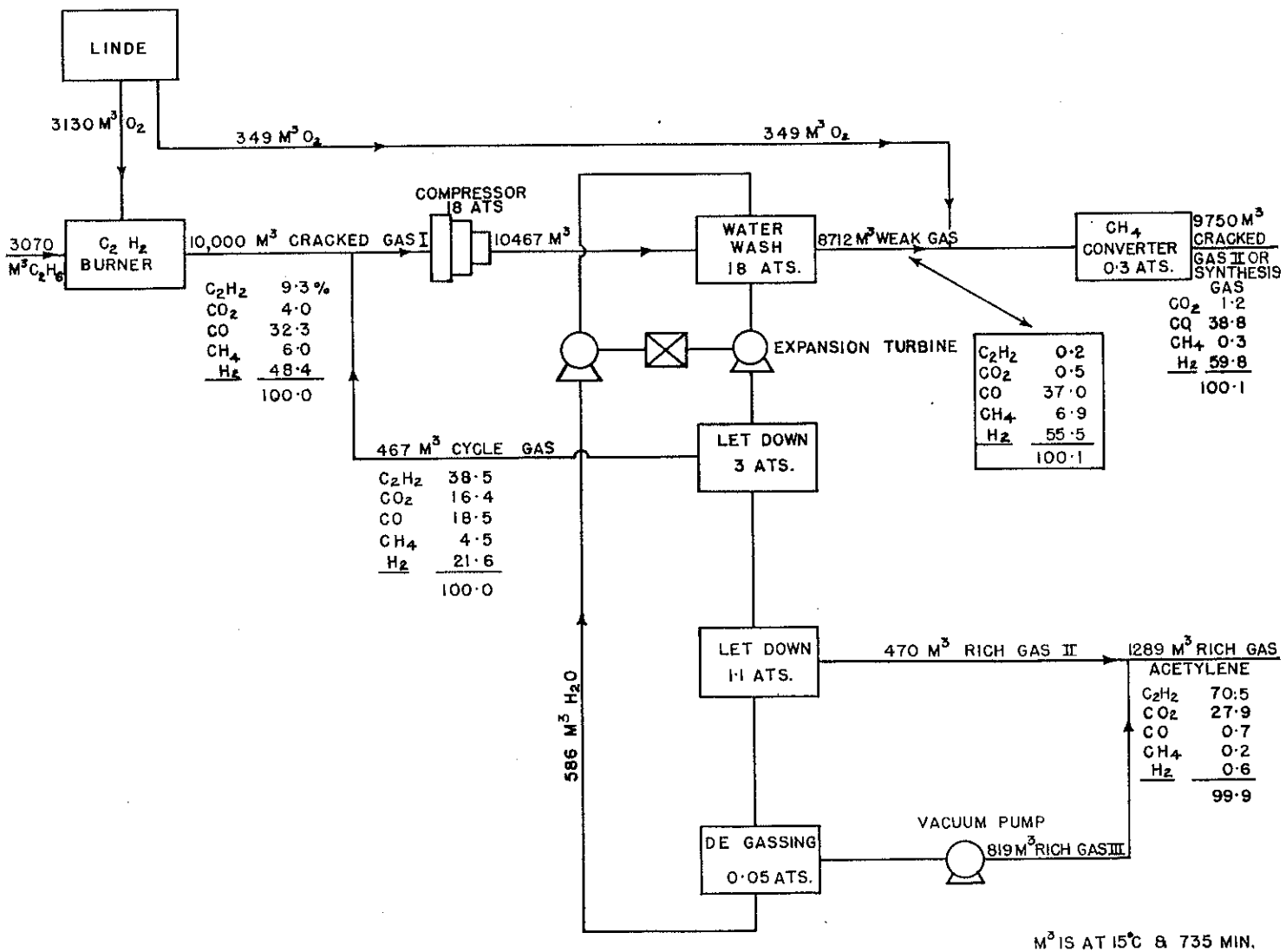
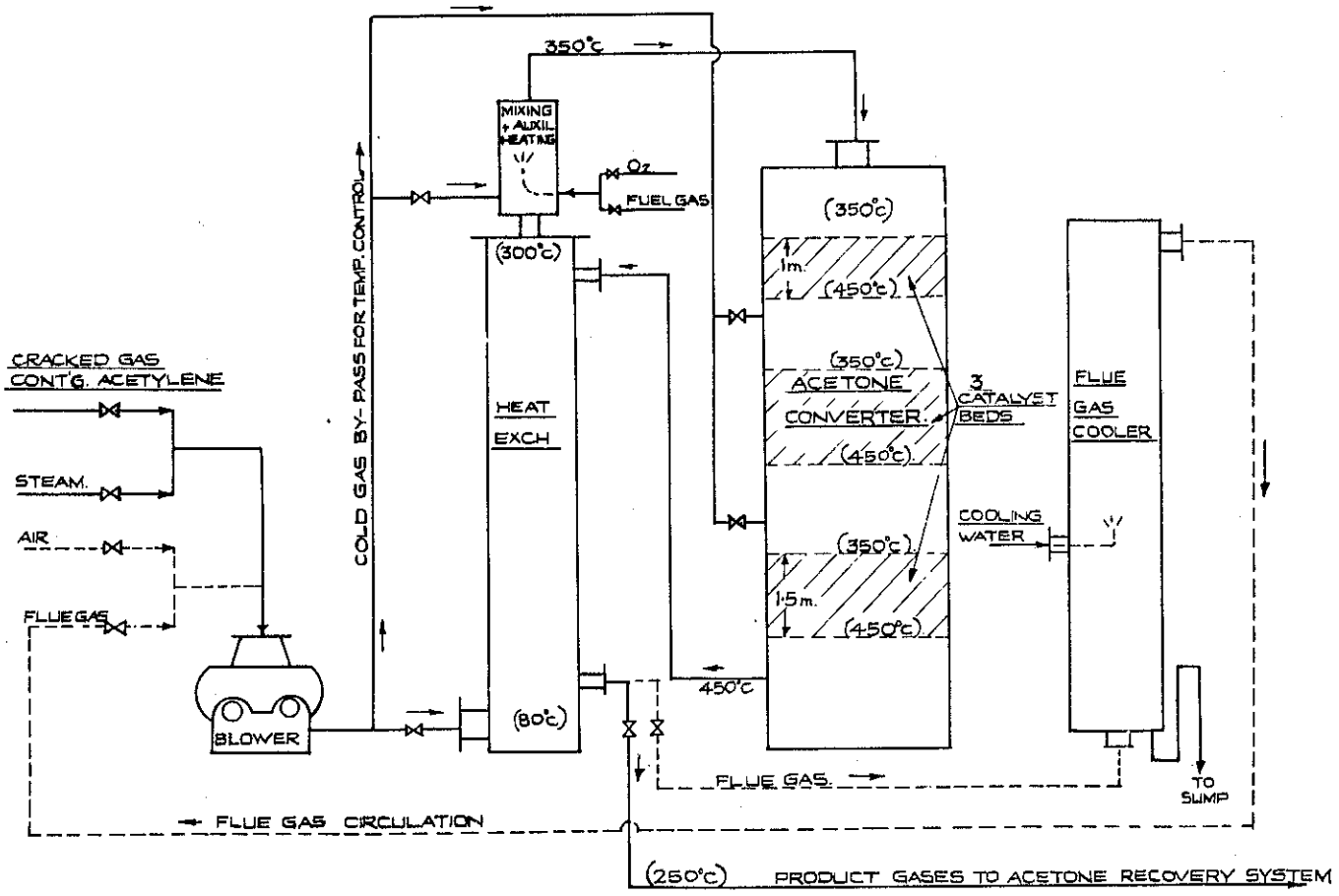


FIGURE X.

K.W PLANT - CONVERSION OF ACETYLENE TO ACETONE.



- - - - - DENOTES F.G. AND AIR LINES, USED ONLY DURING CATALYST REGENERATION.

(REF. SCHEMA. BI. 2)

heaters. When using methane as the feed, the ratio of hydrocarbon to 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 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. VIII. The burning zone has generally a diameter of 700 mm. and a length of 350 mm. and the gas velocity through this zone is 8.5 M/second. A temperature of around 1500° 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% CO_2, 6-7% methane, 24-26% CO and 56% H_2.

(ii) Acetylene Concentration

When concentrated acetylene is required, this exit gas is compressed to 18 ats. and washed with water. The solution of gases in water is let down in two stages - (a) to 3 ats., the gas evolved being recycled to the compressor, and (b) to 1.1 ats. Before recycle the wash water is degassed under a vacuum of .05 ats. Gas obtained in the second let down and in the degassing operation are mixed and this final product contains roughly 70% acetylene and 28% CO_2.

Gas leaving the water washer at 18 ats. contains 50-60% H_2, 35-40% CO and 6-8% CH_4. 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 18-30 ats. More detailed information is desirable.

A flow diagram for the acetylene concentration method is shown in Fix. IX. 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 ethane burning and on the secondary combustion of the synthesis gas.

(iii) Use of Dilute Acetylene for Acetone Synthesis

Another way of dealing with the dilute acetylene adopted by the I.G. is its use for acetone synthesis. Fig. X gives a line diagram of this process.

The acetylene-containing gas is mixed with the required amount of water (steam) and passes through a blower operating at a discharge pressure of 0.2-0.4 ats. The gas mixture is split into three main streams, which are introduced at separate points in the reactor system in order to provide the proper temperature control for the exothermic reaction. The stream charged to the top of the reactor first passes through a heat exchanger and an auxiliary heater where, by means of a fuel/oxygen mixture, the final temperature of this stream is adjusted to 350°C.

This stream then passes through a top bed of catalyst, emerging at 450°C, and is mixed with the second stream (cold gas) with a resulting drop in gas temperature to 350°C. The latter mixture passes through the second catalyst bed, blends with the third stream (cold gas) and flows through the final bed, emerging at 450°C. The hot effluent gas (C_2H_2 content less than 0.2%), after passing through the heat exchanger, proceeds to the acetone scrubbing system, described below.

The catalyst used in this synthesis is zinc oxide in cylindrical pellets 15 mm long x 8 mm diameter. Temperature control is extremely important in preserving the activity of this catalyst, and is complicated by the fact that the reaction rate is also highly sensitive to temperature, e.g. a 2° C rise in inlet gas temperature is claimed to cause a ten-fold, or 20° C rise in catalyst bed temperature. The safe maximum catalyst temperature is about 360°C and the optimum depth of the various catalyst beds is 1 meter in top and middle beds, and 1.5 meters in bottom bed.

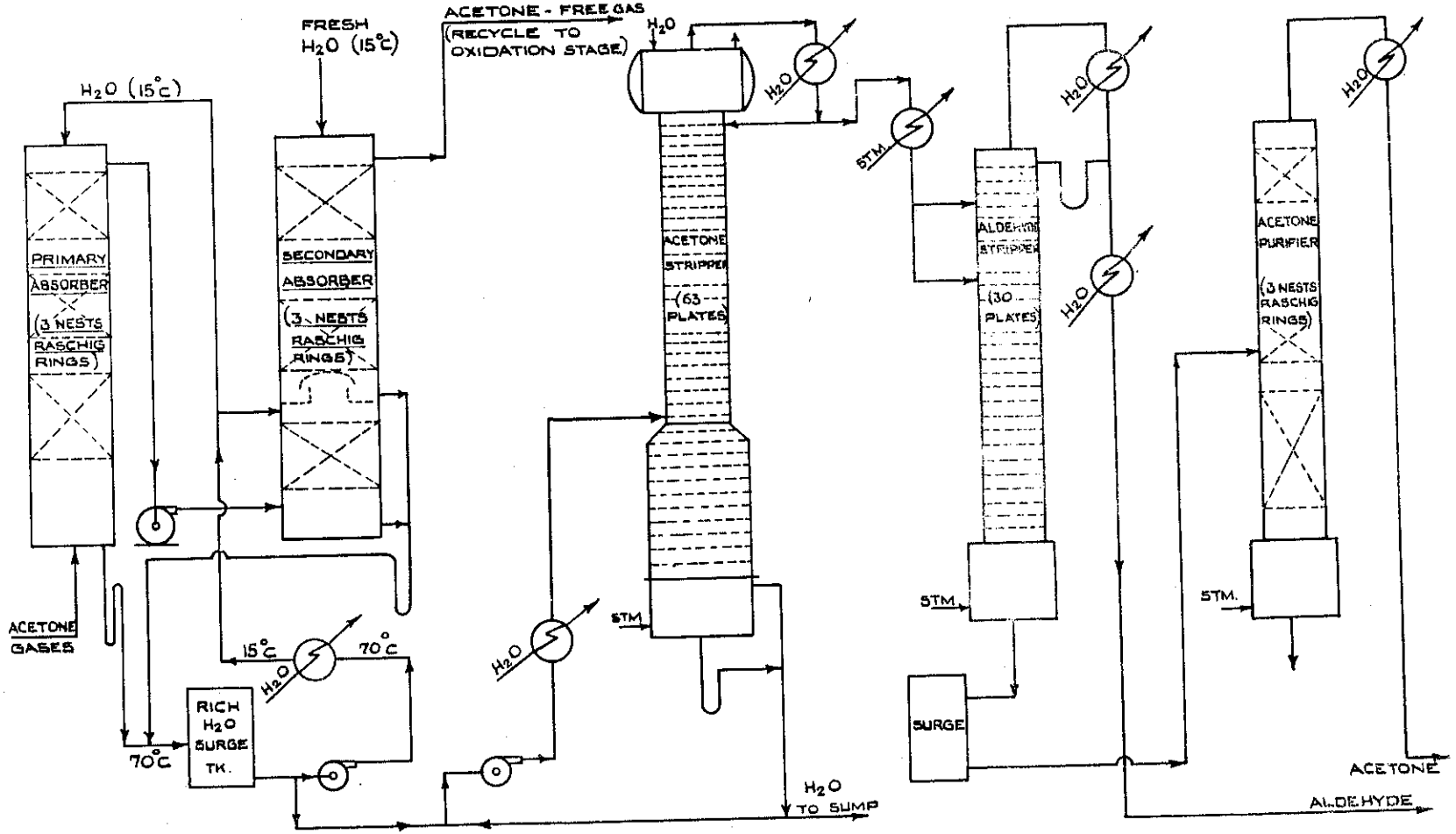
Due to formation of some free carbon, etc. in the synthesis, the catalyst bed gradually becomes fouled, with consequent increase in pressure drop, and requires cleaning every 8-10 days. This is effected by recirculating a mixture of flue gas and air through the converter, maintaining catalyst temperature at 360°C. The flue gas is circulated through a spray cooler. Despite the careful temperature control exercised in this process, however, the catalyst does gradually lose activity, as evidenced by decrease in acetone yield, and requires ultimate replacement about every three months.

The portion of this system dealing with the recovery of the acetone from the product gases is illustrated in Fig. XI. It comprises two pairs of Raschig ring columns in which water is used as the scrubbing agent, a 63-plate stripper column for concentrating acetone, a 30-plate stripper column for fractionating out aldehyde, and a Raschig ring column for redistilling the acetone to final purity. The entire system operates at atmospheric pressure and is of conventional design. The only innovation found in this part of the plant is a new type of absorber recently being tested as a possible improvement over the original Raschig ring column. The experimental tower contains a number of trough-like trays which are mounted on a central rotating shaft, extending the full height of the column. The rotating traps have serrated edges which disperse the falling liquid and provide intimate vapour-liquid contact. Details of this equipment were not obtained.

FIGURE XI

FIGURE XI

KW PLANT ACETONE RECOVERY SYSTEM



NOTE:- ENTIRE SYSTEM OPERATES AT ATMOSPHERIC PRESSURE