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CHAPTER VIII.

DISCUSSIONS AT LUDWIGSHAFEN ON THE PRODUCTION OF SYNTHESIS GAS.

Information was given by

A. Kellogg Company

B. I.G.

C. SHELL.

A. Experiments have so far been carried out in the laboratory only, always having in mind to recirculate the tail gas.

Kellogg's opinion is that probably the largest item in the production cost will be the amortization of the plant. Therefore, it is important to choose the least expensive installation.

The following processes were investigated:

1. CH_4 + O_2 reaction — d.h. = 0,165 m³ O_2/m³ [illegible]

$$CH_4 + \tfrac{1}{2} O_2 \rightleftharpoons CO + 2H_2$$

Temperature 1500 - 1700°F.

Tubes of 3 - 4" filled with catalyst and no difficulties experienced in obtaining a final gas with 1 - 2 % CH_4. (Same results as obtained by Padovani).

A plant was designed having a reactor with 4" tubes in parallel built as heat exchanger, heat to be supplied from the outside. Feed gas to be preheated to 1600°F before entering reactor, as the reactions become endothermic above about 900°C, according to Keith.

This idea was dropped, as calculations showed that the cost of both reactor and oxygen would be prohibitive.

2. CH_4-steam reaction/continuous operations.

$$CH_4 + H_2O \rightleftarrows CO + 3H_2$$

Temperature 880°C.

A plant was designed and calculation showed that the cost of such a plant would be prohibitive. However, this calculation was based on old Standard New Jersey data.

3. Regenerator of 4' dia. using CH_4-steam reaction.

Set up on paper only, based on information from either Bureau of Standards or Bureau of Mines.

Temperature 1800 - 2200°F.

Space velocity on intake gas 200, on exit gas 500.

Designers of such apparatuses informed Kellogg that 1800 - 2200°F is a low temperature for the fire brick available and that it would be possible without difficulties to work at from 2000 to about 2400°F.

Further information on this regenerator:

Cycle of 7 minutes consisting of 3½ min. heating and 3½ min. make periods.

Assumed 15 % excess steam.

Pressure 8 pounds gauge (assumed by Kellogg).

Generator surface 1 m2 for almost 2000 m3 gas.

of regenerator 20', of which 12' filled with catalyst consisting of fire bricks soaked with catalyst (Ni).

Generators of this kind have been estimated by United Gas Improvement Company, U.S.A., to be of lower cost than the estimates mentioned under 1. and 2.

B. Information given by Dr Schiller, one of the inventors of the methane steam process as applied by us at Pernis for production of hydrogen.

In the years of 1925 - 1930 much work was done by I.G. on the production of hydrogen from hydrocarbons in connection with hydrogenation work, NH_3 production, etc.

1. Methane steam process.

Temperature 650 - 750°C.

Found catalysts for this reaction. Afterwards also catalysts were discovered for the conversion of higher hydrocarbons (for instance, tail gas of hydrogenation plants) and olefine-containing gases.

I.G. have or had a pilot plant in Oppau.

2. CH_4 - O_2 reaction.

$$CH_4 + \tfrac{1}{2} O_2 \rightleftarrows CO + 2H_2$$

This equation is purely theoretical; actually many other side reactions take place. Reaction is incomplete and CO_2 is formed also. Reaction investigated in pilot plant having a capacity of 100 m3 CH_4/hour. Roughly this pilot plant consists of a burner to which CH_4 and O_2 are fed together with a little water. Reaction product and unconverted CH_4 and O_2 enter at about 1300°C a layer of brickwork, which is followed by a layer of catalyst. Temperature of product at exit of catalyst about 800°C. Gas mixture entering catalyst layer still contains about 5 - 8 % CH_4 and leaving the catalyst 1 - 2 % CH_4.

Basic for the CO_2-formation is the well-known watergas equation:

$$CO + H_2O \rightleftarrows CO2 + H_2$$

As the production of CO_2 by this equation is favoured by lower temperatures it is Dr Schiller's opinion that it is better not to use a catalyst for this reaction ($CH_4 + O_2$ conversion) when producing gas for Fischer synthesis. In that case, however, somewhat more O_2 will have to be used in order to obtain a final gas with not more than 1 - 2 % CH_4.

<u>Example</u>:

Temperature 1300°C. 100 m3 CH_4 + 60-64 m3 O_2 gave:

33 % CO
58 % H2
4 % CO_2
~~1 % CH_4~~
rest N_2

The advantage of operating without catalyst was found by accident. The process is simple, but it is evident that the price will be determined mainly by the cost of O_2.

Burner constructed in such a way that O_2 is supplied tangential.

3. $CH_4 + H_2O \rightleftarrows CO + 3H_2$

The watergas reaction plays an important rôle in this process. Therefore, very high temperatures have to be used in order to obtain a gas with only small amounts of CO_2.

This process gives a CO-hydrogen ratio of at least 1 : 3.

4. $CH_4 + CO_2 \rightleftarrows 2CO + 2H_2$

gives a CO-hydrogen ratio of 1 : 1. By carrying out the CH_4 steam and CH_4-CO_2 reaction simultaneously the right and desired proportion of CO to H_2 can be obtained. The overall reaction for producing a gas with a ratio $CO : H_2 = 1 : 2$ is as follows:

$$3CH_4 + CO_2 + 2H_2O \rightleftarrows 4CO + 8H_2$$

However, in order to complete the reaction an excess of CO_2 and steam is necessary, leaving the CO_2 excess in the final gas to an extent of about 5 - 6 %. About 50 % of excess steam is required. In this case no or almost no carbon will be formed.

Catalyst same as for the CH_4-steam reaction.

Although this reaction can be carried out discontinuously with catalyst, Dr Schiller believes that ~~the continuous method with catalyst is to be preferred.~~

Space velocity with catalyst 1000 m3 H_2 + CO/hour per 1000 l contact volume, possibly even with 800 l contact volume. These are figures for the H_2 production by the CH_4-steam reaction.

Contact volume when working without catalyst is much higher. However, these figures were obtained by Dr Schiller from the literature only, for instance, 1000 m3 H_2 + CO/hour per 50 m3 reaction volume. This seems to be very high, but Dr Schiller does not believe that one could come below 10 - 20 m3 contact volume.

Laboratory figures illustrating the above reaction in continuous operation with catalyst at 750°C are:

$$\left.\begin{array}{l} 260 \text{ m3 } CH_4 \\ 140 \text{ m3 } CO_2 \\ 190 \text{ kg } H_2O \end{array}\right\} \longrightarrow 1000 \text{ m3 gas having}$$

= 14 % CO_2 !

following analysis:

CO	30 %
H_2	60 %
CO_2	6 %
CH_4	2 %
N_2	2 %

Dr Schiller believes that such figures can certainly be obtained in a large-scale plant.

I.G. have a pilot plant with a capacity of 100 m3 CH_4 per hour which has been running now for about 3/4 of a year.

When considering this process the question arises how to produce CO_2. An obvious method would be to start with flue gas, as this usually contains 7 - 10 % CO_2. However~~,~~ although it can be separated from this by absorption it is believed that this will certainly not be cheap.

Another way would be when hydrogen is produced at the same time for hydrogenation purposes.

Several processes are being investigated at the moment for the production of CO_2 by I.G. Although Dr Schiller does not want to divulge any information already at present it is his belief that CO_2 can be made directly from methane cheaper than by absorption from flue gas.

The above reactions can also be carried out with hydrocarbons obtained in hydrogenation processes. Such hydrocarbons are usually the mixture of CH_4 up to and including C_4H_{10}. However, somewhat different catalysts have to be used in that case.

Information given by Dr Sabel from Leuna

At Leuna the I.G. are investigating the production of synthesis gas or hydrogen in regenerators (Cowpers) without catalyst. As feed gas hydrogenation tail gases are used consisting of 60 % hydrogen and a hydrocarbon mixture with the general formula

$$C_{2.2-2.3}H_{6.4-6.6}$$

These experiments confirm Dr Schiller's data.

With 50 - 60 % excess steam at 1300-1400°C (at the hottest places) gas can be produced consisting of:

11 -12 % CO
77 - 78 % H_2
1 % CH_4
rest N_2 and CO_2

Production of carbon cannot be avoided in this case. Sometimes 5 - 6 g carbon per m3 synthesis gas is formed. Part of the carbon remains in the gas, giving difficulties in the purification and even in the synthesis. Therefore, chambers between the generators were built in and O_2 added at this spot to burn the carbon. Notwithstanding this, a small amount of carbon, say, about 100 - 200 mg per m3, remains in the watergas.

Dr Sabel believes that it is quite possible to avoid all carbon when using larger generators. The present two generators each have a cross-sectional area of ½ m2 and a height of 8 m. With better insulation it will also be possible to obtain higher temperatures.

Run figures:

1 m3 gas + 1/10 - 2/10 m3 O_2 (all normal m3) + 3 kg steam, gives 3½ m3 watergas (see analysis). These figures are not binding.

A Cowper of 8 m height produces 1000 m3 watergas/m2/hour. Increasing this height will probably result in a higher output.

Experiments have been made in which CO_2 has been added. In this case a good proportion of CO and H_2 could be obtained. However, the total percentage of CO + H_2, being 88 - 90 with steam only (see above), is decreased to 75 - 78 %.

Brickwork in the highest temperature zone consists of silimanit. This brickwork can still be used at 1400°C.

C. Information was given by SHELL (Dr Langen van der Valk) on the Shell Point methane reformers as according to Kellogg's calculations such process when applied with the addition of steam and CO_2 looks the most promising for the production of synthesis gas in the U.S.A.

The Reforming Plant at Shell Point has three generators; total cost of these generators including brickwork at the time of building, about $ 275,000.

The following operating figures over one month of 30 days were given:

	1000 cu.ft (60°F 14.73 lbs)	m3 (0°/760 mm)
Natural gas intake:	157,569	4,223,000
Reformed gas production:	250,283	6,710,000
Gas for fuel:	18,156	487,000
Heat consumption:	4,020 x 10^6 kcal = 600 kcal/ m3 reformed gas	

Total steam consumption of the entire gas reforming plant :	3,528,000 lbs/month = 1600 t = 0.24 kg/m3 reformed gas
Power consumption	
Gas Reforming Plant:	94,000 kWh
Average temperature:	at top of generator 2000°F at centre of " 2060°F

Each of the generators has a diameter of 20' and a height of 55'. They work on a heat and make period in 20 min. cycles.

Data on such cycles are:

	min.	average rate per minute.
Heat period	5½	waste gas 530 cu.ft air 13,400 cu.ft
Purge	2	steam ± 110 lbs
make period	11½	gas 2400 cu.ft
Purge	½	steam ± 110 lbs
Purge	½	air 13,400 cu.ft

Gas analyses of the feed gas, the gas produced and the rest gas are as follows:

	Natural gas	Gas produced	Rest gas
CO_2	-	-	-
C_nH_m	-	1.3	4.9
O_2	-	0.1	0.1
CO	-	1.7	3.2
H_2	-	71.3	2.2
CH_4	76-	23.2	83.1
C_2H_6	22.7	0.8	2.0
N_2	1.3	1.6	4.5
Calorific value kcal/m3			
upper limit	± 10900	± 4750	± 9130
lower limit	9840	4170	8250

The gas produced after leaving the generator contains a large amount of carbon, which is removed by passing the gas through wash boxes filled with water which lowers its temperature at the same time to about 60°C. Further cooling of the gas is done by means of two towers with direct water cooling.

It was mentioned that Shell Point also has an experimental generator with a capacity of about 55 cu.ft natural gas per minute.