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THE SCHMALFELDT PROCESS
FOR MAKING SYNTHESIS GAS
FROM METHANE

BY

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FIAT FINAL REPORT 1305

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ABSTRACT

This report is a translation of a document by Hans Schmalfeldt dated March 29, 1947, describing work done in the plant of Klocknerwerke, A. G., Castrop-Rauxel, Germany, on the production of synthesis gas from methane containing gases by non catalytic reaction with steam and oxygen. In a pilot plant built in 1931, coke oven gas was converted under a pressure of 23-24 atm. abs. with air enriched to 33 per cent oxygen. Methane in the exit gas was less than 1 per cent and no soot formation was observed. The maintenance of the refractory lining proved quite difficult.

A larger plant, started in 1938, could not be operated until 1941, because of difficulties in getting materials, particularly refractory brick. Results were not entirely satisfactory because of inadequate heat recovery and the lack of facilities for purging unreacted gas between cycles. Fischer-Tropsch residue gas and coke oven gas were converted at a pressure of 8-9 atm. abs. with an oxygen consumption 30-40 per cent above theoretical and with only slight formation of soot.

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I. INTRODUCTION

Considerable information has been published about the Schmalfeldt process for lignite gasification which is named after its German inventor, Dr. Hans Schmalfeldt. Dr. W. F. Faragher, Chief of the Fuels and Lubricants Unit of FIAT, discussed this subject briefly with Dr. Schmalfeldt in December 1946 in the course of selecting certain German experts to write summary reports on various aspects of the Fischer Tropsch Process. As a result of this discussion, Dr. Schmalfeldt revealed that he had also directed considerable research on the production of synthesis gas from methane containing gases by reaction with oxygen and steam. At Dr. Faragher's request Dr. Schmalfeldt prepared a report on this work which was received in May 1947. Subsequently there was no opportunity to discuss this report with Dr. Schmalfeldt to obtain additional information. However, the report seemed to be of general interest and therefore, it has been translated and the translation is reproduced on the following pages.

The German original has been forwarded to the Office of Technical Services, U. S. Department of Commerce, and it will be reproduced on Technical Oil Mission Microfilm Reel 238 from which copies may be obtained if desired, through the Library of Congress.

A brief description of the same process was included in a report by C. C. Hall and A. R. Powell, entitled Plant of Klocknerwerke, A. G., Castrop-Rauxel Germany, reprinted by the Office of the Publication Board, U. S. Department of Commerce as Report PB 286.

II. START OF DEVELOPMENT

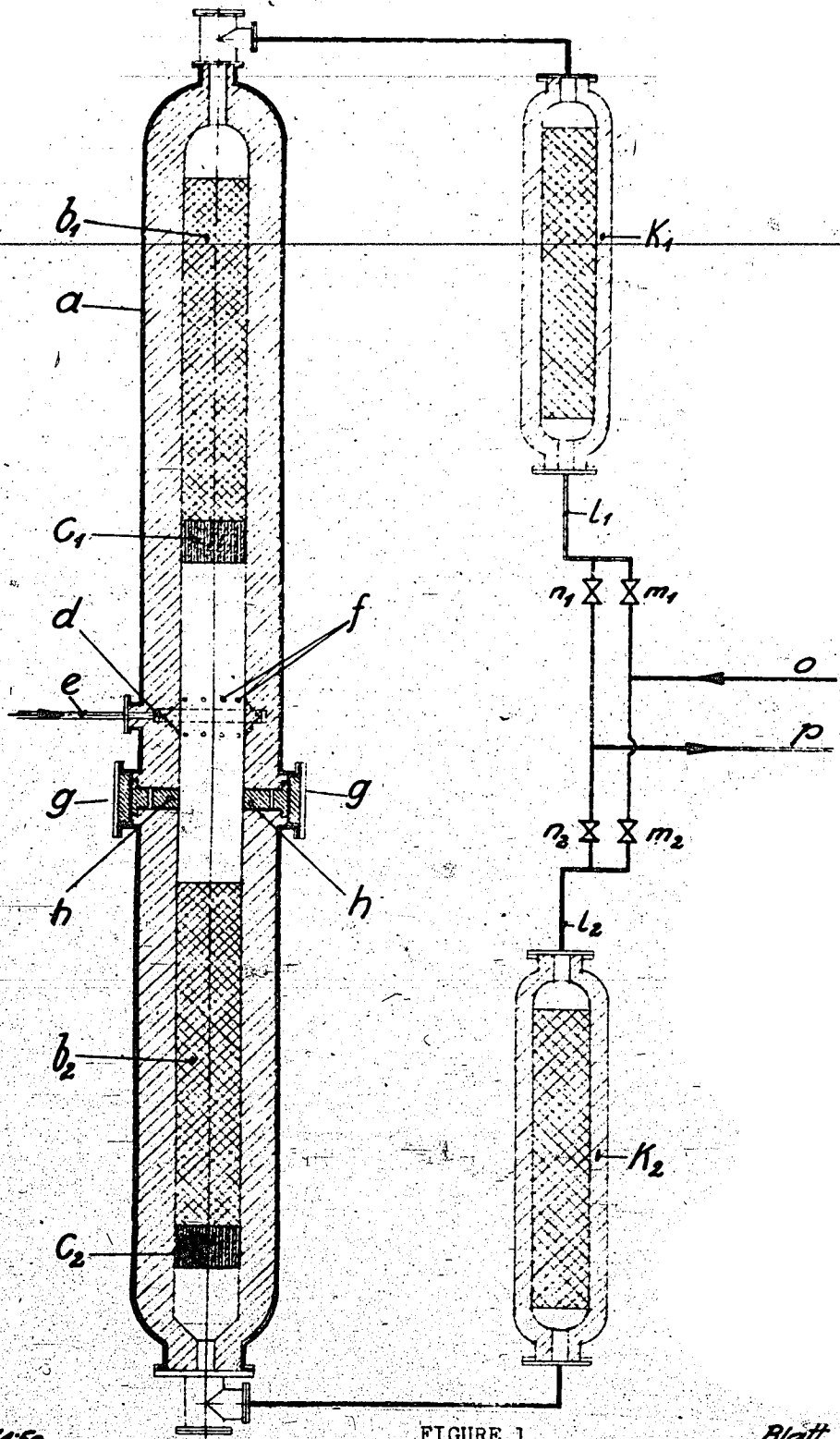
At the time the nitrogen plant was being constructed the Victor Company was already involved in the famous Bronn-Concordia case. The chemist, Bronn, together with Berkwerkgesellschaft Concordia Mining Company, were engaged in a lawsuit over the rights to the gas separation process which had been licensed to Victor by L'Air Liquide, claiming sole exploitative rights to the separation of coke oven gas by means of pressure and low temperature. The case was lost by Victor in the lower courts and taken to a higher one. Grave danger existed that the plant would be completely shut down by the litigants. For this reason the possibilities of producing hydrogen from coke oven gas by other means than pressure and cold were explored. These investigations pointed up the problem of separating the hydrocarbons in the coke oven gas into hydrogen and carbon monoxide and then, if possible, of converting the carbon monoxide into hydrogen and carbonic acid. Further, it appeared desirable to undertake the conversion of the hydrocarbons with the pressure supplied by the coke gas compressors, namely, a pressure of about 25 atm. abs. because this operational procedure could best be adapted to production routine, and in this manner economies in

compression costs could be effected.

Since it was not feasible to supply reaction heat by purely regenerative means under pressure because the stone blocks, in general, are too bulky, a decision was taken to try a combination, that is, to work partly by regenerative means and partly by the addition of oxygen. ~~The combination of these two was of additional interest because oxygen requirements would have become excessive without heat exchange between incoming and outgoing gases.~~ On the other hand, a recuperative heat exchange is not practical because of the high temperatures involved. Finally, a decision was made to work without catalysts, that is, to develop a purely thermal operating procedure because, in the Claude process, the coke oven gas is compressed and passed into the scrubber while still unpurified or before desulfurization. Therefore, under some circumstances the pressure splitting of methane would probably be placed between compressors and scrubber.

III. INITIAL EXPERIMENTAL EQUIPMENT

On the basis of the above-mentioned requirements and considerations, an experimental apparatus illustrated by Figure 1, page 3, was conceived, worked out, and gradually completed in the years 1930 and 1931. The original apparatus consisted of a pressure-resistant reactor (a) of 1300 mm. total diameter and about 12-1/2 meters in length. This reactor was lined with fire-proof bricks 450 mm. thick, consisting of a Sterchamol insulating layer outermost, and two fire-proof layers of fire brick and Mullital. The inner diameter of the remaining shaft was 400 mm. The upper and lower thirds of the empty space were packed with two fillings (b₁) and (b₂) of pieces of Mullital brick about 40 - 60 mm. in size. Both brick packings rested on fire-proof grates (c₁) and (c₂). The inlet for the oxygen-containing gases was situated at about the center of the remaining third. Two small circular channels (d) located in the wall were connected with the oxygen-containing gas inlet (e) and the oxygen-containing gases were passed into the reaction vessel through individual holes (f). With the aid of auxiliary burners the reactor was intensely heated, reaching red heat in the central section so that coke oven gas and oxygen were ignited on meeting. Construction problems in pre-heating before the start of operations were not successfully solved. Openings measuring 200 mm. had been made at diametrically opposed points (g) in the wall just below the oxygen inlets. Before heating the apparatus a gas burner was introduced into these openings from both sides. The flue gases were sucked out at both ends of the apparatus by a small auxiliary ventilator, which operated only during heating periods, and were then vented. As soon as the central section of the apparatus was heated to red heat, the auxiliary burners were withdrawn in order to protect the walls at this point from excessive temperatures. Two brick plugs (h) were then inserted from outside and the covers screwed on.



M150

FIGURE 1
SCHMALFELDT METHANE CRACKING PILOT PLANT

Blatt I

When it became apparent that heat exchange was not quite satisfactory, two more pressure-resistant reactors (k_1) and (k_2), each measuring 700 mm. in total diameter, were added in the manner indicated in Figure 1. The walls of these two reactors were less heavily lined and also possessed an inner diameter of 400 mm. Heat exchange was then effected by means of perforated bricks of barely 400 mm. total diameter, which had been installed. At the ends of the apparatus, that is, at (l_1) and (l_2), the gases were conducted to the regulating valves. At each end were situated valves (m_1) and (n_1) and valves (m_2) and (n_2) for the incoming and outgoing gases. Since it had not been possible to install an automatic switching device in this short period of time, these valves were regulated by two men who operated the switches at intervals of five minutes which were measured by an hour glass.

Roughly 525 - 550 cbm/hour of coke oven gas to be decomposed were admitted into the inlet pipe (o) together with a volume of steam about three times the amount required for complete methane conversion. These amounts were permanently controlled by gas and steam meters and maintained at a constant value with sufficient accuracy. The exit pipe (p) leading out of the apparatus conducted the converted coke oven gas together with the excess water vapor through a heat exchanger for the purpose of heating the incoming gases to about 250 - 300°C. The exit temperature was between 300 and 350°C, whereas the incoming temperature of the gas-steam mixture ran to about 200 - 250°C. Since no steam at a pressure of 25 atm. abs. was available on the spot, a small auxiliary boiler for this pressure was installed for the experiments. The air-oxygen mixture was preheated to about 300°C. in two parts by a small superheater.

After a series of experiments with the actual cracking apparatus, a further experimental step was taken in that an apparatus for conversion of the carbon monoxide was installed beyond the cracking apparatus. In this manner it was planned to obtain a finished synthesis gas for the ammonia synthesis in one pass. It turned out, however, that the exit temperature from the cracking apparatus was too low for the carbon monoxide catalyst to be effective. For this reason a small intermediate superheater was temporarily introduced which heated the gas about 50 - 60°C. to reach 400° so that the conversion could be accomplished. The intermediate superheating was accomplished by heating a short V2A tube. It was clear that the temperature could have been regulated without the use of intermediate superheating and the requirements for the subsequent conversion could have been fulfilled. This could have been done by an appropriate arrangement or by tapping the cooler apparatus ends and by drawing off a warm partial steam.

IV. OPERATIONAL RESULTS

All copies of the exhaustive documents relating to the pilot plant have unfortunately been destroyed or lost as a result of war damage. The most essential facts must therefore be reconstructed from memory. However, ~~this can be done with satisfactory accuracy. As has been already~~ mentioned, 525 - 550 cbm. of coke oven gas with a triple volume of water vapor were charged hourly, that is, with about 700 kg. per hour of water vapor. There was pressure of 23 - 24 atm. abs. in the reactor, the exit temperature running from 300 to 350°C. A mixture of air and oxygen was admitted as the oxygen-containing gas. The oxygen content of the gas used for the reaction ran to about 31 per cent in the beginning and slowly increased to 33 per cent because the construction of the passages through the heating tubes was faulty. Heat losses were incurred to an increasing extent and finally incandescent spots appeared. The synthesis gas mixture amounted to about 1100 - 1200 m³/hour with hydrogen and nitrogen in a 3:1 ratio when employing a pre-heated coke oven gas of the following composition:

57% H₂
26% CH₄
4% C_nH_m, mostly C₂H₄ and C₂H₆
6% CO
7% nitrogen

and air with 31 per cent oxygen. The methane content of the finished gas was 0.5 - 1 per cent and the carbon monoxide content was 0.5 per cent.

It should be mentioned that a double conversion took place in the last period of operation, the final synthesis gas being experimentally admitted into the synthesis plant. After the first conversion the carbonic acid was washed out and, after an intermediate superheating, the gas was again converted. This last measure was taken in order to prove that it was possible to reach the point where the finished gas could be directly used for the synthesis by actually "cracking" the hydrocarbons and converting the carbon monoxide. A carbon monoxide scrubber would take the place of the second converter in the practical execution of the process, but it was simpler to convert the gas once more during the experimental work.

Temperatures in the hotter sections were taken by platinum-platinum-rhodium thermoelements. Thermoelements were installed in many spots. The jacket temperatures of the pressure-bearing reactor were also controlled, namely, by means of iron constantan elements. Maintenance of the thermoelements during operation was extremely troublesome. Since trouble had been expected from the very beginning, installations were so arranged that thermometers could be readily replaced at the hot spots. Thermal measurements showed temperatures at the hottest points of about 1400°, for

the most part, with temperatures of 1450° being reached at some points.

It is noteworthy that no carbon appeared in the plant. Whereas formation of 4 - 8 g. of carbon for every cbm. of cracked gas may be expected in purely regenerative decomposition without pressure, no carbon formation was noticed in the pressure apparatus. Since the carbon monoxide in the outgoing gases was converted beyond the cracking apparatus for a period of 8 days, carbon should eventually have appeared at the very least on the carbon monoxide conversion catalyst. This catalyst was very dense, was divided into small particles and was sharp-edged so that any carbon formation must have been disclosed on examination of the catalyst mass after the experiments. However, examination of the catalyst did not disclose any carbon formation.

V. EXPERIENCES WITH THE CRACKING APPARATUS ITSELF

In planning the apparatus it was quite evident that special attention had to be paid to the construction and selection of the refractory lining. To this end collaboration was instituted with the Didier company. Since Didier likewise possessed no experience with similar apparatus, a brick-work was recommended by this firm for the hottest areas which turned out to be too weak. In addition, it turned out that at those spots where the heating burners had been placed, the wall had been markedly weakened by the perforations bored in it. Also, the introductions of the plugs after heating did not furnish any real insulation for the flange neck. Accordingly it did not take very long before the layers of Sterchamol in the vicinity of the openings could no longer stand the temperature, melted, and red hot areas appeared on or in the vicinity of the perforations. As long as the red hot spots were no larger than a hand's breadth they were sprinkled with water and the apparatus was shut down after the last continuous experiment when heat losses became too great.

Experience with the pilot plant showed that a reactor operated at these temperatures must have stronger walls, above all, that the Sterchamol layer cannot take temperatures that are too high and, finally, that the installations employed for heating the converter must be modified. Most important of all, it is absolutely essential that perforations of such size in the hot areas be avoided.

VI. RESUMPTION OF THE PROCESS

After thoroughly satisfactory results had been obtained in the pilot plant, and after errors in the construction of the wall had become clear, the operation of the pilot plant was discontinued and the separate parts, especially the pressure-resistant walls, were used elsewhere. Primarily operations were not continued because the Bronn-Concordia case was finally

won in the upper courts, and the danger of a shut-down of coke-gas fractionating operations were thus averted. The problem of converting methane-containing gases under pressure was again tackled in 1938 when the problem of better utilization of the residual gases of the Fischer-Tropsch plant was being dealt with. At that time the proposal was offered in a report dated April 25, 1938 that 4500 cbm. of residual gas containing 25 - 30 per cent of hydrocarbons (the heavy hydrocarbons being converted to methane equivalent) should be converted with oxygen and water vapor. About 6000 cbm./hour of a new synthesis gas were to be prepared therefrom and this new synthesis gas was again to be converted in 5 - 6 Fischer pressure reactors. Just at that time the Fischer-Medium Pressure Synthesis appeared and was received favorably everywhere. It was obvious also to the Gewerkschaft Victor that they should carry out an experiment with this modification of the Fischer-Tropsch Process on a small scale for the purpose of improvement of plant operation.

VII. CONSTRUCTION OF A PLANT

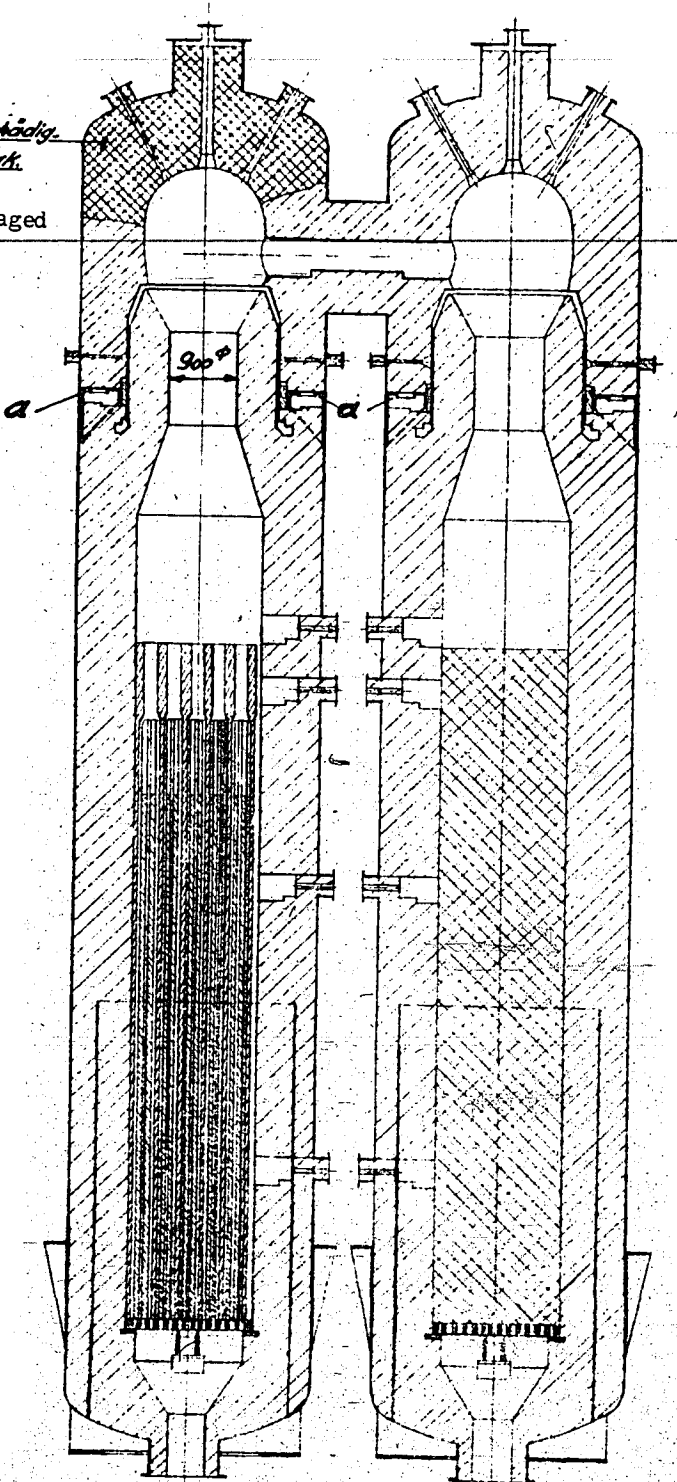
The plant arrangement contemplated two converters which were to be joined together. Since the converters were to be placed upright, consideration had to be given to wall expansion in view of the large dimensions involved. In order to avoid a flaring out of the cupolas, as in the case of large regenerators for pressure heating of large volumes of gas, and, in addition, to furnish a solid support for the upper cupola wall with concurrent expansion possibilities for the jacket wall, a new cupola support was designed as shown by Figure 2, page 8. The cupola was placed on a heavy cast iron ring (a) which was protected against the most intense temperatures by an extension of the inner wall. It was thereby impossible to avoid a contraction of the inner diameter at this spot. However, it was thus possible to anchor the cupola securely and to maintain the smooth cylindrical shape of the pressure-bearing outer jacket. Oxygen-intake was provided for by 6 inlet nozzles situated at the top of each converter.

The cupolas were always the hottest parts of the converters because of the oxygen intake. It was also necessary to join the converters at this part in the area of the greatest heat. However, this did not cause any trouble. The wall itself was considerably stronger than the pilot plant wall, being thicker by about 750 mm. and the cupola, into which the oxygen stream- ed, had refractory walls that were even stronger. Normal hexagonal Schiffer-Strack bricks were selected for the lining, the upper 5 layers consisting of bricks perforated with one hole and the lower layers of bricks with several holes. A cast iron grate was provided as a support for the lining.

The problem was concurrently posed of washing a portion of the carbonic acid from the residual gas of the Fischer-Tropsch synthesis. Since no scrubber of sufficient size was available for this purpose, but two smaller

*Zweimal beschädig-
tes Mauerwerk.*

Twice damaged
wall



M1-75

FIGURE 2
LARGE SCALE METHANE CRACKING REACTORS

Blatt II

ones were available which would do if employed jointly, the gas current was conducted in parallel through these two carbonic acid scrubbers.

A humidifying and dehumidifying plant was installed in order to conserve steam. Thus, the overall gas circulation was as shown by Figure 3, page 11. Compression of residual gas by means of compressor A of 5000 cbm./hour capacity at a pressure of 9 - 10 atm. gage, scrubbing of carbonic acid in 2 carbonic acid scrubbing towers connected in parallel (B₁) and (B₂) of 2200 mm. total diameter humidifying with circulating hot water; and then addition of the remaining steam and admission into the regulating apparatus, that is, into the alternately used inlet valves (E₁) and (E₂). For instance, if the gas which is to be converted enters through (E₁) into converter (K₁), it will flow through the upper connection into converter (K₂) and will pass the escape valve (F₁) (sic.) into the outlet pipe and from there into the dehumidifier (G) and into the final cooler (H). From (H) the gas should flow into the medium pressure reactors. The humidifying and dehumidifying chambers (C) and (G), as well as the final cooler (H), were combined in one lengthy cylindrical vessel. The complete plan is illustrated in Figure 3, page 11. All the valves were automatically regulated by means of air, the cycle periods generally lasting about 7 minutes.

Oxygen was passed into the plant under pressure by means of a small compressor of about 450 - 500 cbm. capacity and then introduced into the cupola of each converter by means of 6 nozzles. Provisions had also been made for regulation of the oxygen intake. It was therefore possible to supply a continuous steady stream of oxygen to both cupolas or to supply the oxygen to the connection between the cupolas, thereby supplying that converter with oxygen into which the gas flowed through the connecting pipe from above. The oxygen nozzles were made of a double tube of heat-resistant steel through the center of which flowed the oxygen. A volume of cool steam flowed through the annular space. This cooling steam volume was measured for both converter halves together to be about 300 - 400 kg./hour. The oxygen could also easily be diluted with a small amount of steam.

Heating was conducted by means of a gas burner introduced through the look boxes into the upper parts of the centers of each of the cupolas, both converters thereby being simultaneously subjected to intense heat. The flue gases were again sucked away by an auxiliary ventilator.

For the hot area a good silica material was selected as brick material. The upper part of the packing also consisted of silica quality. For the cooler areas material of inferior quality was chosen. The lower layers of the packing and of the wall were constructed of normal fire brick.

The inner diameter of the brick wall was 1650 mm.. In the area of the cupola support (see Figure 2, page 8) the diameter narrowed to 900 mm..

This contraction, which was designed for the protection of the cupola support, at the same time promoted commingling and diffusion of the gases. The diameter of the iron jacket was 3150 mm. and the overall length was 18,400 mm. The height of the lining was 10,700 mm.

Originally it had been intended to obtain a packing of rather large surface area. The surface area of the normal Schiffer-Strack bricks is really insufficient. For this reason various proposals were made to brickware companies, particularly to the Dr. Otto company in Bochum, with reference to a packing with a rather large surface area. However, since the brick industry at that time was very rushed, the brick firms showed little interest in view of the smallness of our order. There was nothing for it but to finally turn to the normal Schiffer-Strack bricks. It also turned out that exit temperatures during operation were too high and that it would be necessary to lower them. Since it became apparent at the same time that the carbonic acid wash was not necessary, especially in view of the fact that only later was the processing of coke oven gas considered to be of primary importance, both carbonic acid scrubbers were also walled and provided with packing so that they now served as extensions of the converters. The circulation of the gas was now as follows: Admission into a walled carbonic acid scrubber, entrance into appropriate converter from below, overflow into the top of the second converter, discharge from the bottom into the second carbonic acid scrubber and thereafter into the regulating apparatus. The carbonic acid scrubbing towers were also equipped with the normal Schiffer-Strack bricks for their packing since, as was already mentioned, possibilities for obtaining larger surfaced bricks at that time were non-existent.

VIII. OPERATIONAL EXPERIENCES WITH APPARATUS

Unfortunately the methane pressure cracking plant from the very beginning and even during operation was under the influence of an unlucky star. The construction of the plant was proposed in the early part of 1938. The first difficulty popped up when it turned out that all orders would take a long time to fill because of the press of business in the industry. Orders for the pressure-resistant reactors, for instance, were placed under great difficulties. The same held for residual gas and oxygen compressors. At first it was only possible to procure an oxygen compressor of 400 - 500 cbm./hour and the second one which was somewhat larger, having a capacity of 600 cbm., was delivered so late that it was not possible to put it into operation. The trouble in procuring suitable packing bricks has already been related so that, as far as this important part of the plant was concerned, it was necessary to employ unsuitable material from the very beginning. Furthermore, as a result of the pressure of business on the part of the companies, it was impossible to install the recording and control instruments necessary for an initial plant. Above all, a suitable instrument for rapid recording of the methane contents in the converted gas was missing. Pro-

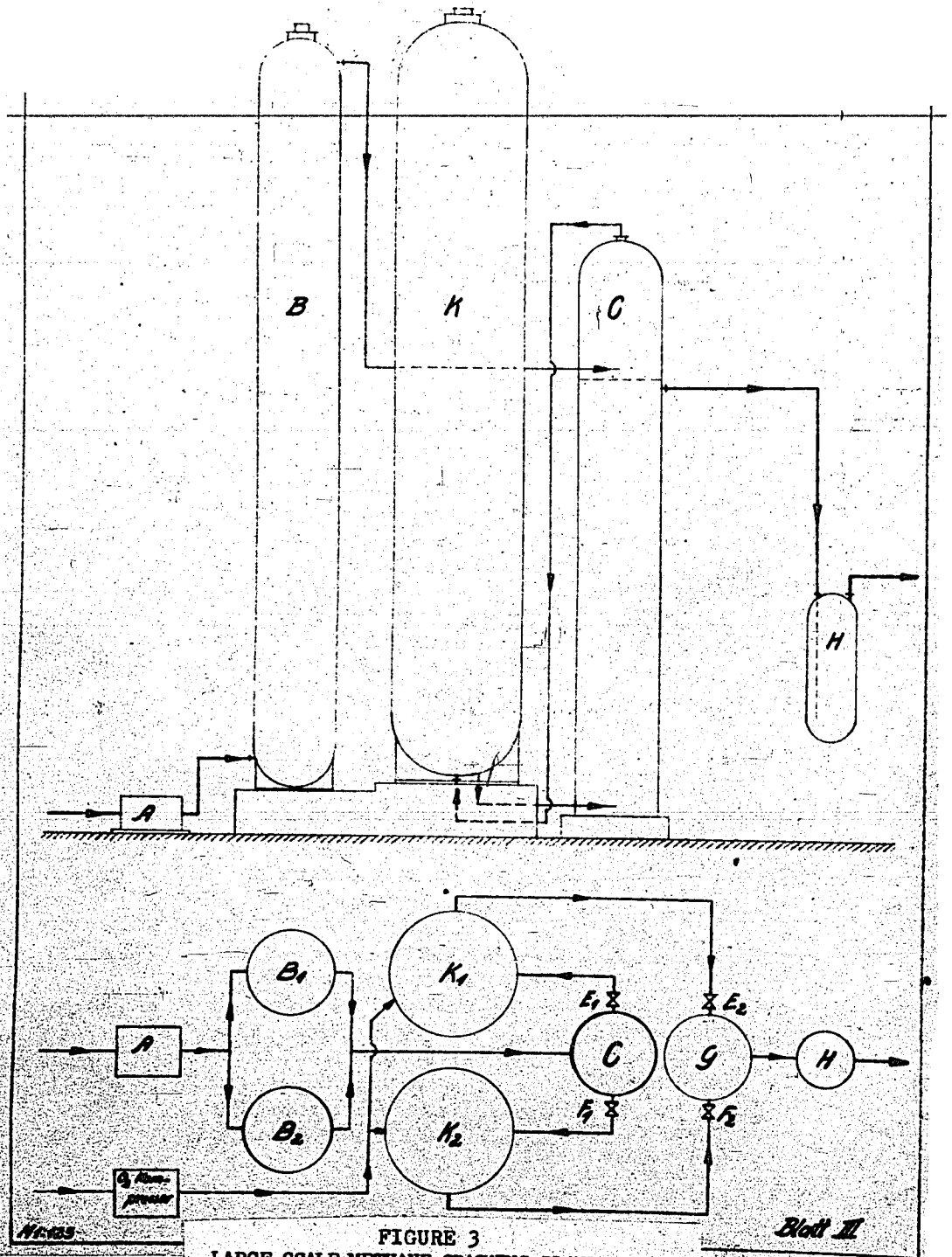


FIGURE 3
LARGE SCALE METHANE CRACKING PLANT LAYOUT

jects for the construction of such indicating devices which promised success were conceived but could unfortunately not be carried to a successful conclusion.

It turned out to be especially unfortunate that the original plans for reacting the finished gas again in 5 - 6 Fischer medium pressure reactors could not be carried out because of the outbreak of war. Thus, the principal reason, which had originally determined the cracking of the residual gas under pressure, disappeared, that is, because it was originally also desired to operate the added pressure reactors as a third stage under the cracking pressure at the same time. With the discontinuance of the pressure reactors, pressure cracking more or less lost its economic justification, in any case, for the immediate future. The gases which were to be converted were compressed quite unnecessarily since they were finally used without pressure.

As a result of the procurement difficulties already mentioned, operation of the plant was postponed until the middle of 1941. The shortage of men and materials which was beginning to be felt at that time had a pronounced effect on the pressure cracking plant which no longer seemed so necessary because of the discontinuance of the pressure reactors. Therefore, it came to be regarded more or less as a pilot plant and, in addition, as a pilot plant whose findings were not regarded as absolutely necessary for the immediate present. This general attitude prevented the pressure cracking plant from being planned and operated with the care that should have been absolutely necessary for a new plant of this kind. In addition, difficulties which arose could not be averted and the necessary improvements and repairs could not always quickly be attended to because of the shortage of personnel and often of material. As a result the whole project dragged and was extremely vexing.

When operations first started it became evident that the packing which consisted of normal Schiffer-Strack bricks of relatively small surface area, would not suffice to attain sufficiently high exit temperature and a consumption of oxygen which would not be excessive. For this reason, as has already been described, both carbonic acid scrubbing towers of 2200 mm. total diameter were also walled and furnished with normal Schiffer-Strack bricks in order to increase the exchange area by this means. After a period of operation in May, June, and July of 1941 the plant had to be shut down because of damage to the fire-proof wall of the cupola of one of the two converters. Repair work dragged on for a long time and it was only by May of 1942 that operations could be resumed. However, at the end of June the same trouble occurred again to the same converter. The cupola was again repaired and the oxygen intake (see below) was changed. However, because of troubles connected with the war and because it was not absolutely essential to put the plant in operation, the plant was not set in operation again. When

the plant was finally ready it was struck by bombs and seriously damaged.

It is very curious that the damage to the cupola wall (see cross hatching in Figure 2, page 8) occurred both times in the same converter, in the same place and in the same way, whereas the other converter remained completely uninjured. In this connection, attention must be paid to the fact that both converters worked under exactly the same conditions and, while one converter twice suffered severe damage in the upper section, the other suffered no damage whatever. The reason for this singular occurrence is probably to be found in the fact that the cooling steam, which was blown into the annular chamber around the oxygen nozzles at the rate of 300-400 kg./hour and which served to prevent overheating of the refractory inlet tubes, was evidently not supplied to one of the converters. The cooling vapor was measured with a steam meter and then distributed through the two valves into the two converters. The valves were disproportionately large for the small volume of vapor involved so that it could never be determined with certainty whether the valve was already open or whether the turning of the hand wheel was lost motion. Subsequent investigations disclosed that it was highly probable that the steam valve was closed in the twice-damaged converter and only the slack was turned so that no cooling steam had been passed in around the oxygen nozzles. As a result the entire amount of steam has always been on tap for the other converter. As a result of the lack of cooling steam the forepart of the heat-resistant tube had been burned off and the flame had approached the wall too closely. The wall had then begun to melt away and was furthered by the iron flux. A little more of the inlet nozzle was again burned away and in this manner the cupola wall was gradually melted away.

Despite the acknowledgement of the fact that only an unfortunate accident could have caused the twofold damage to the converter, it was decided to extend the oxygen inlet. Although the oxygen supply had hitherto been automatically controlled and passed into that converter into which the gases from the other converter flowed in from above, it was now decided to furnish an oxygen intake for both cupolas and, at the same time, to lighten the load in both cupolas by providing radially placed oxygen nozzles in the wall. In this manner the heat load in the upper conversion spaces, that is underneath the cupolas could have been reduced from $1/4$ to $1/3$ of the original load. Unfortunately however, the completed alterations were not put into use because the plant, as has been mentioned, was no longer operated.

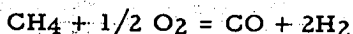
Practical experience has shown that direction of the oxygen supply is not necessary although, in this connection, it must be recalled that there was no oxygen direction in the first pilot plant. On the other hand it turned out that installation of a steam purge was absolutely essential for satisfactory operation. Before reversing the current of gas the still unconverted or not completely converted gas mixture can be forced by the steam purge

from the colder parts of the apparatus into the hotter areas where they are converted. When the circuit is switched shortly thereafter, large amounts of unconverted gas cannot be entrained with the flue gas. These devices were about to be installed when work was stopped as a result of the war. This important point will again be discussed below.

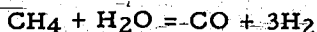
It turned out to be extremely unfortunate that the provisions made for oxygen compression were so inadequate. Only one compressor of 400-500 m³/hour was available but because of the delicacy of this compressor it could not always be run at full capacity. For the purpose in view it was absolutely essential to have a volume of 800 - 1000 cbm. oxygen available (see below).

IX. PROCEDURAL AND CHEMICAL OPERATIONAL EXPERIENCES

The conversion of methane with oxygen or oxygen and steam is often represented in this form:



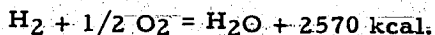
This representation is not quite accurate. The actual course of the decomposition of methane with oxygen depends on numerous subsidiary factors, the principal ones being the composition of the wet gases, the temperature and the heat losses during reaction. Conditions are susceptible to exact calculations to some extent with certain assumptions, as has been demonstrated by comparisons of calculations and results. However, the calculations are too complex for rough estimate; the course of the reaction must therefore be represented in a simplified manner as follows. Methane is decomposed with water, thus



This reaction is endothermic to the extent of 2350 cal./m³ methane with stoichiometric proportions. The oxygen blown in has to contribute the reaction heat. The oxygen can either burn the carbon monoxide to carbonic acid or the hydrogen to water vapor, thus

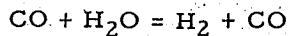


or

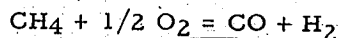


The liberated quantities of heat are again related to 1 cbm. of charged combustible gas. If all heat losses were disregarded, then 0.78 m³ of carbon monoxide would be converted to carbonic acid in the case of exclusive oxidation of the carbon monoxide in order to supply the reaction heat for the decomposition of 1 m³ of methane with water vapor. If only hydrogen is

burned, 0.92 m³ of hydrogen would be required to maintain the heat balance. It is assumed that equal parts by volume of hydrogen and carbon monoxide oxidize, then 0.95 cbm. of this gas mixture would have to be available. As things really are, everything depends on the composition of the starting material to be reacted with water vapor. It is clear that the water-gas (shift) reaction plays a prominent role, the reaction proceeding as follows.



As was already mentioned, the actual volume of oxygen which must be employed can be calculated with sufficient accuracy if the governing equilibrium above all the water gas equilibrium, is determined. However, it is clear from the above that the reaction does not proceed exactly according to the formula



On the other hand it is clear, however, that 0.39 to 0.46, averaging 0.425 m³ oxygen are required for the conversion of 1 m³ methane according to prevailing conditions.

Heat losses play an important role in this process, as can be demonstrated by a simple calculation. It is assumed that a gas containing 25 per cent CH₄ is reacted, with a 95 per cent conversion. Simple decomposition with water vapor would then require 0.25 x 0.95 x 2350 = 560 kcal. Further, if a triple volume of water vapor, calculated with respect to methane, is assumed, then the volume of converted gas formed from 1 m³ of dry gas is 1 + 0.75 + 0.71 = 2.46 cbm. If the converted gas now leaves with a temperature 100 degrees C higher, than that of the gases entering the reaction vessel, then a heat loss of 2.46 x 100 x 0.33 = 81 kcal. occurs for every 1 m³ of methane containing gas. On the basis of the size of this apparatus a further calculation may be made to the effect that an additional 60 kcal per 1 m³ of charged dry gas must be used as a result of heat losses from the apparatus due to radiation and conduction. In this manner the figures of the following table have been worked out, the first column representing the difference between exit and entrance temperature, the second column denoting total heat expenditure to be made up through oxygen addition, and the third column representing that factor with which the theoretical heat or oxygen expenditure must be multiplied in order to obtain the practical heat or oxygen expenditure related to the theoretical figures.

TABLE I

<u>Difference Between Exit and Entrance Temperature °C.</u>	<u>Total Heat Expenditure, kcal.</u>	<u>Factor</u>
100	701	1,25
200	782	1,40
300	863	1,54

It is thus apparent that oxygen consumption increases markedly as the exit gas temperature increases. Twenty-five per cent more heat is consumed in the case of temperature difference of 100 degrees between outgoing and incoming gases than correspond to the theory. At 200 degrees it is about 40 per cent and at 300 degrees it is 54 per cent naturally always under the conditions of the assumed example. Roughly estimated, it can be seen that in the above three cases oxygen consumption for the conversion of 1 cbm. of methane is of the order of 0.53, 0.6 and 0.67 cbm. of oxygen.

Unfortunately almost all figures and documents relating to the pressure decomposition plant were destroyed or lost as a result of war damage. On the basis of reconstruction of conditions from memory and from the scanty remaining documentary material which was accidentally saved, the following information can be offered with reasonable accuracy:

The cracking of residual gas from the gasoline synthesis was next tried. In this connection the insufficient supply of oxygen was as troublesome as in all the other experiments. Above all the insufficient capacity of the oxygen compressors together with the lack of a purge when the converter was reversed resulted in the yield often dropping to 50 per cent. It was only seldom that it increased to 70 per cent, corresponding to a residual methane content in the decomposed gas of 8 per cent down to about 4 per cent. A number of typical analyses from 1941 with Fischer residual gas are shown in Table II, page 17.

The quantity of converted gas is not known exactly because of the absence of documentary material. However, about 3500 - 4500 cbm. of residual gas was processed. Moreover, it is evident that the carbonic acid scrubber was necessary, for a portion of the carbonic acid is again converted into carbon monoxide with attendant hydrogen consumption. According to the analyses performed, yields ran to about 70 per cent. Further, experiments were conducted to process coke oven gas. However, the daily analyses of the charged coke oven gas can no longer be ascertained; therefore, the monthly mean analysis was employed for comparisons. Since there was little day to day variation in the composition of the coke oven gas, a relatively accurate

TABLE II

<u>Date</u>	<u>Kind of Gas</u>	<u>H₂</u>	<u>CO</u>	<u>CH₄</u>	<u>C_nH_m</u>	<u>N₂</u>	<u>CO₂</u>
17.6. 1941	Cracked Gas	35,1	18,8	4,9	0	19,5	21,5
	Residual Gas	19,8	13,0	19,7	1,8	19,9	25,8
18.6.	Cracked Gas	35,4	17,4	5,7	0,1	19,0	22,2
	Residual Gas	19,8	11,0	20,2	1,7	19,4	27,8
19.6.	Cracked Gas	34,2	18,0	4,9	0,2	19,3	23,2
	Residual Gas	19,7	11,6	19,6	1,5	19,3	28,2
20.6.	Cracked Gas	33,9	19,7	4,2	0,1	18,8	23,2
	Residual Gas	18,1	12,1	20,5	1,9	18,9	28,5

picture can be obtained. These experiments also occurred in 1941, the charged volume of gas being 2000 - 3000 m³/hr.

TABLE III

<u>Date</u>	<u>Kind of Gas</u>	<u>H₂</u>	<u>CO</u>	<u>CH₄</u>	<u>C_nH_m</u>	<u>N₂</u>	<u>CO₂ Yield</u>
5.7. 1941	Cracked Gas	66	13,2	7,8	0,2	7,5	5,1
	Coke Oven Gas	54,9	5,6	23,9	2,2	9,7	2,4
6.7.	Cracked Gas	66,5	13,1	7,2	0,2	7,8	4,8
	Coke Oven Gas	54,9	5,6	23,9	2,2	9,7	2,4
7.7.	Cracked Gas	67,9	13,5	6,2	0,3	6,4	5,5
	Coke Oven Gas	54,9	5,6	23,9	2,2	9,7	2,4
8.7.	Cracked Gas	65,0	12,9	7,9	0,4	7,7	5,7
	Coke Oven Gas	54,9	5,6	23,9	2,2	9,7	2,4

The rich gas from the coke oven gas decomposition of the nitrogen apparatus was also subjected to pressure cracking. The following figures resulted from the mean values of an operational period extending from May 22, to May 30, 1942

TABLE IV

Kind of Gas	H ₂	CO	CH ₄	C _n H _m	N ₂	CO ₂
Cracked Gas	51,5	15,9	9,4	0,4	12,6	10,1
Rich Gas	14,4	12,9	47,6	3,1	21,4	0,2

On the basis of the nitrogen contents the conversion in this series of experiments can be readily calculated, C_nH_m being added to methane in double amount. A conversion of 68 per cent is obtained. The finished gas was again put at the disposal of the nitrogen plant for decomposition into hydrogen and rich gas, about 2000 m³/hour of residual gas being thereby converted.

On the basis of rough estimates at that time it was figured that the oxygen consumption of the plant, on the basis of 1 cbm. of converted methane, would be about 30 - 40 per cent above theoretical requirements. A similar calculation for the considerably smaller pilot plant, which operated in 1931 under a pressure of 25 atm. abs., resulted in an oxygen consumption of 0.76 cbm. for 1 cbm. of methane which was accordingly about 80 per cent more than the ideal of no-loss conversion.

An attempt was made to do without addition of steam to the charge gas and to admit all the steam in the humidifying plant. This was not entirely successful so that increasingly scantier volumes of steam were added to the split gas in the order of several hundred kilograms per hour. The entire steam consumption of the plant ran to about 1 - 1.5 tons per hour. The steam added to the incoming gas, the cooling steam for the oxygen nozzles, and the steam added to the oxygen intake were covered by this. These figures are naturally not definitive for a well run plant. No reason can be seen why the steam consumption of a cracking plant operating under pressure should be larger than that of a pressureless plant. On the contrary, since water vapor is formed during conversion of a portion of the finished hydrogen, outside steam should be conserved so that the above process should really require less steam than a normal pressureless cracking plant for hydrocarbons.

The very important exit temperature of the gases leaving the apparatus ran to 230 degrees C., whereas the entrance temperature of the humidified gases varied between 130 - 145 degrees C. The temperature difference therefore did not amount to more than about 100 degrees C. From this it is apparent that the plant could have handled a much higher charge rate if sufficient oxygen had been available. Furthermore, if the extremely unsuitable Schiffer-Strack checker bricks had been replaced by a more appropriate packing which would have possessed less free space due to greater surface area, the performance of the plant could have been appreciably stepped up.

Whereas the volume of methane actually converted ran to 650 - 800 m³ of methane in all instances, this volume of methane could have been multiplied if suitable packing and sufficient oxygen supply had been provided, namely, to a volume of methane of 2000 - 3000 cbm. per hour.

~~The unfortunate effect of the missing purge shortly before switching becomes evident through an investigation which was conducted by a sample of the converted gas being withdrawn at one minute intervals after the switch, as shown by Table V.~~

It can be seen from the last experimental series, for instance, that the cracking left as little as 1.2 - 2 per cent methane. Nevertheless, the unconverted quantities of gas from the cooler parts of the apparatus markedly increase the average of analyses with respect to the methane content. It is from this point of view that all analyses, which are given above, and all prolonged analyses in excess of at least 8 hours, are to be evaluated. If the purge had been introduced shortly before the switching the methane contents arrived at would have been a fraction of those which were actually found to be mean values, and the decomposition yields would not have been 50 - 70 per cent, but rather 75 - 95 per cent.

It is thus clear that purging before switching is just as necessary in the case of a pressure plant as in a pressureless plant. Whereas, in the case of pressureless apparatus the unconverted gas as well as the flue gas must be purged, in the case of a pressure plant a single purge during the reversal period will suffice, to force the still unconverted gases into the hot part of the apparatus. This arrangement can be easily made from the point of view of apparatus. An automatically controlled purging valve is the only device which must be provided.

As far as that goes, in the first pilot plant, which was operated without purging this phenomenon had as yet not had an unfavorable effect. The methane content which was then obtained, was between 0.5 and 1 per cent, and even lower in part. On the other hand, the free spaces of the apparatus were appreciably smaller. This referred mainly to the subsequently added auxiliary regenerators into which the gas was first passed. The packing of these regenerators was furnished with evenly fitting cylindrical bricks of 400 mm. diameter, having a number of relatively narrow perforations which were flooded with gas. The unsuitable Schiffer-Strack bricks with which the plant was equipped and, above all, the subsequent addition of packed former carbonic acid scrubbers with their large free spaces, had a markedly bad effect on the average analysis of the cracked gas. As a result of the installation of the auxiliary regenerators, too much unconverted gas was carried along into the mean analysis during switching.

TABLE V

Date	Time When Sample Was Taken	CO	H ₂	CO ₂	O ₂	N ₂	C _n H _{2n}	CH ₄	Number	H ₂ CO
16.6. 1941	1. Min.	13,0	20,2	26,4	0,4	21,0	0,4	18,6	1,16	1,55
	2. Min.	13,4	28,6	31,0	0,2	19,0	0,4	7,4	1,00	2,14
	3. Min.	16,9	33,0	28,0	0,1	17,6	0,0	4,4	1,14	1,95
	4. Min.	17,7	34,7	25,0	0,1	17,2	0,0	5,3	1,00	1,96
	5. Min.	18,1	34,0	24,6	0,1	17,2	0,2	5,8	1,07	1,88
	6. Min.	18,6	34,0	23,7	0,1	17,3	0,0	6,3	1,14	1,83
	7. Min.	18,4	33,6	24,4	0,2	17,8	0,0	5,6	1,07	1,83
	8. Min.	18,5	33,9	24,0	0,2	17,7	0,0	5,7	1,02	1,83
16.6	1. Min.	12,2	21,3	25,6	0,1	22,0	0,4	18,4	1,10	1,75
	2. Min.	14,5	31,0	30,2	0,1	19,2	0,2	4,8	1,08	2,14
	3. Min.	18,5	36,6	23,6	0,0	17,5	0,1	3,7	1,03	1,98
	4. Min.	19,6	37,2	22,2	0,2	17,4	0,2	3,4	1,12	1,90
	5. Min.	19,3	37,4	22,2	0,1	17,0	0,0	4,0	1,08	1,94
	6. Min.	19,4	36,8	22,4	0,1	17,3	0,1	3,9	1,0	1,90
	7. Min.	20,3	37,6	20,0	0,1	18,0	0,0	4,0	1,15	1,85
18.6	1. Min.	13,5	23,5	26,2	0,4	19,8	0,0	16,6	1,10	1,74
	2. Min.	12,2	27,0	33,2	0,1	19,0	0,1	8,4	1,07	2,21
	3. Min.	16,1	33,6	30,2	0,2	17,4	0,1	2,4	1,16	2,09
	4. Min.	18,4	38,6	24,3	0,2	16,6	0,1	1,8	1,22	2,10
	5. Min.	19,3	39,1	23,6	0,3	16,5	0,0	1,2	1,25	2,03
	6. Min.	20,5	38,2	23,6	0,2	16,1	0,0	1,4	1,07	1,86
	7. Min.	20,6	38,3	23,6	0,0	16,1	0,0	1,4	1,00	1,86
	8. Min.	19,8	38,6	23,2	0,4	16,0	0,0	2,0	1,10	1,95

Carbon formation also presented an interesting picture during operation of the plant at 8 - 9 atm. abs. It turned out, however, that carbon formation had not been completely suppressed, as in the case of the 1931 pilot plant, but that an appreciable decrease of carbon formation could be recorded as compared with a pressureless plant. Whereas a pressureless cracking plant gives 4 - 8 g. or more of carbon for each cubic meter of cracked gas, as has been measured again and again in the case of the pressureless plants available, this plant produced only 0.344 g. carbon for every cubic meter of cracked gas at an average pressure of 9 atm. abs. On a volumetric basis, only a twentieth of the carbon was formed as compared with pressureless plants:

In order to avoid carbon formation completely or almost completely, it was necessary to work with pressure higher than 9 atm. abs., namely with a pressure equivalent to that of the 1931 pilot plant, that is, about 20 atm. gage and higher.

X. SYNOPSIS, DIRECTION OF DEVELOPMENT, AND POSSIBILITIES FOR USE

The following conclusions were reached on the basis of operations with the 1931 pilot plant as well as with the larger one during 1941-1942:

1. The process can be recommended for large-scale commercial use.
2. Oxygen consumption per cubic meter of converted methane will range from about 0.55 to 0.65 cbm. oxygen, depending on conditions and quality of the plant.
3. Carbon formation at pressures of 20 atm. gage and over will be more or less completely avoided; in the case of lower pressures it will drop to a small fraction of the quantities customary in pressureless operation.
4. If the apparatus is suitably constructed conversions of 90 - 95 per cent can be attained.
5. Particularly careful attention must be paid to the oxygen intake; in this connection it is desirable that the oxygen supply be distributed in the direction of the gas stream so that local overheating can be avoided.
6. Measures must be taken to render the unconverted or partially converted gases inactive during reversal, namely by keeping the spaces in the colder parts of the apparatus small or by a brief purge before switching, or by a combination of both methods.
7. A packing with relatively large surface area must be provided.

In constructing new plants one can either maintain the upright method of construction, whereby numerous improvements based on experience and on newer considerations can be made, or a horizontal method of construction

which possesses many advantages, can be developed. Studies have also been initiated on this score.

Furthermore, it is possible to convert the plant for catalysts, chiefly when the conversion of sulfur-rich gases is involved. There are definite ideas on this subject, too.

It is further possible to add another pressure conversion after the conversion of the hydrocarbons, in which case it is advantageous that carbon formation can be extensively or almost entirely suppressed. This requirement must be made if a carbon monoxide conversion is to be added because otherwise the converter catalyst will undergo pronounced carbonization and will become ineffective, or will clog the apparatus, and the withdrawal of large quantities of carbon will create marked difficulties.

This process can be applied everywhere that methane-containing gases under pressure are available and must be further worked up under pressure or, in those cases where the starting gases are available without pressure, but where the cracked gas is afterwards required under pressure. Natural gases, Fischer-Tropsch residual gases, distillation gases, etc. can be used as starting gases particularly for the production of synthesis gas for the medium pressure Fischer-Tropsch synthesis, for hydrogenation hydrogen, methanol synthesis et cetera.

Rauxel, March 29, 1947

Schmalfeldt

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