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TECHNICAL REPORT NO. 556-45.

METHANE CRACKING BY PARTIAL COMBUSTION

WITH OXYGEN OR AIR IN GERMANY

OCTOBER 1945

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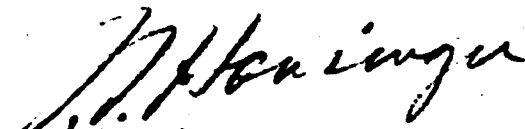Serial: 1635   31 October 1945

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TECHNICAL REPORT NO. - 45

METHANE CRACKING BY PARTIAL COMBUSTION WITH OXYGEN OR AIR

IN GERMANY

Summary

This report records information obtained by technical investigators on processes for the cracking of methane in coke oven gas and of pure methane by the partial combustion with oxygen or air in Germany for the production of hydrogen, hydrogen-carbon monoxide mixtures, hydrogen-nitrogen mixtures and acetylene.

The report describes several processes and the factors controlling them. The emphasis has been upon those parts of the processes which are not common in the United States, the more common elements having been omitted. The appendix contains flow diagrams and copies of selected original German documents pertinent to the subject, which serve to elaborate on the chemical engineering phases and the development of the processes.

August 1945

U.S. NAVAL TECHNICAL MISSION IN EUROPE

RESTRICTED

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INTRODUCTION

In spite of the scarcity of hydrocarbons in Germany it has been only since the beginning of the war that the Germans have developed and brought into large scale use, processes for converting the common methane or methane-containing gases into hydrocarbon products suitable for chemical purposes. Until comparatively recently coke oven gas, as well as residual hydrogenation Fischer-Tropsch residual gases were only processed in Germany to recover by absorption the propane and heavier components, the remaining methane and ethane being then used principally for fuel gas. During, or just prior to the war, experiments were carried out on the cracking of these gases to yield feed gases for other important processes. As a result of this work several processes have been developed and commercial scale plants built and put in operation in Germany. One method, the Häuber Process for ethane cracking was developed by I. G. Farbenindustrie in Leuna and is discussed in a Naval Technical Mission report on Aviation Gasoline. Another, the direct Electric Arc cracking process for producing acetylene from methane, was developed and put into operation at the Hüls plant of I. G. Farbenindustrie and is the subject of another Mission report. This report is therefore limited to a consideration of the cracking of methane by partial combustion with oxygen or air.

I. G. Farbenindustrie at Ludwigshafen, the Lurgi Company at Frankfort and H. Koppers Company at Essen have worked on this problem, and several commercial scale plants using the processes have been built and put in operation. The commercial installation at the Oppau works of I. G. using that company's process was inspected and Dr. Sachsse and Dr. Kosbahn were interrogated. Documents were also obtained from the Lurgi Company. A Koppers process installation was inspected at Rheinpreussen, Dr. Karl, Dr. Ackeren, Dr. Daniels and Dr. Koppers were interrogated at the Koppers offices, and documents were obtained.

The partial combustion of methane can be utilized for the production of useful products by two general processes designated by the type of products made as follows: (I) Either carbon monoxide-hydrogen mixtures for the Fischer-Tropsch, methanol etc syntheses or a nitrogen-hydrogen mixture for the ammonia synthesis, and (II) Acetylene plus the synthesis gases in I. This report treats these in separate sections due to the widely different combustion conditions required.

(I)   SYNTHESIS GAS PRODUCTION BY PARTIAL COMBUSTION

Methane oxidizes to produce carbon monoxide and hydrogen according to the following three equations:

(1) $CH_4 + CO_2 \longrightarrow 2 CO + 2 H_2$

(2) $CH_4 + H_2O \longrightarrow CO + 3H_2$

(3) $CH_4 + 1/2 \, O_2 \longrightarrow CO + 2 H_2$
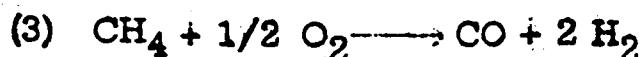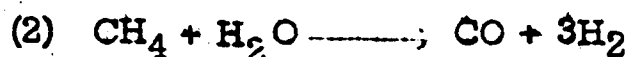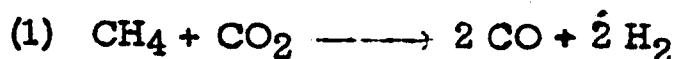
To obtain a favorable equilibrium and rate in any of these three reactions a temperature of over 800°C must be used with a catalyst (or over 1000°C. if no catalyst is used). The first two reactions are endothermic and the third is exothermic. Therefore, by using a process carrying out reaction (3) simultaneously with one or both of the other reactions, the necessary endothermic heat for the first two reactions is supplied directly in the process and the problems of heat transfer equipment at high temperatures and the difficulties of pressure operation are largely avoided. In addition, by varying the relative extent of the three reactions in the combined reaction process adopted, close control can be easily maintained over both the $CO:H_2$ ratio of the product and the temperature of the reaction.

In this section two processes are described for the production of synthesis gases by partial combustion. The first one, employed by I. G. at Oppau, is a continuous process employing a nickel catalyst. The second one is an intermittent or regenerative cycle operation without a catalyst.

(A) Partial Combustion with a Nickel Catalyst

A flow sheet for the production of synthesis gases by partial combustion of methane in a gas mixture with a nickel catalyst is shown by Drawing Op 631 N-Sch 1 in the appendix to this report. This flowsheet (and the equipment shown thereon) can be employed to produce either an ammonia synthesis gas mixture or various carbon monoxide-hydrogen mixtures for such syntheses as methanol, isobutanol, Fisher Tropsch, etc. The principal difference in the process for producing these two types of gas mixtures is that when the need is for gas for the ammonia synthesis, part of the oxidation or combustion oxygen is obtained by using air instead of pure oxygen to the extent necessary to yield a ratio of $N_2:H_2$ of 1:3 in the final gas.

In the flow-sheet for synthesis gas production the coke-oven gas

is first saturated with water at about 70°C. This is shown in Item 11. It is next preheated to about 500-600°C in the gas preheater Item 13, and then goes to the burner in the upper part of the combustion chamber, Item 15. The controlled amount of oxygen (or air) similarly saturated with water in Item 12, is preheated in Item 14 and is then mixed with the gas at the burner. Combustion takes place initially at about 1200°C, but the temperature becomes reduced to about 1100°C. due to the endothermic reaction with the water present. At this temperature the gas passes down through the Nickel-on-Magnesite catalyst situated immediately below the combustion chamber, leaving the bed at about 900°C. The outlet gas is first used to preheat the incoming feeds, is next cooled to 85°C. by direct contact with water in Item 17, and is passed through a coke "Schacht" filter Item 18 for removal of the carbon formed during the decomposition. The gas is next cooled in a heat exchanger Item 19 and passed through an iron oxide box Item 20 for H_2S removal. After the sulfur is removed the gas passes back through the other side of the heat exchanger. It is lastly passed through a direct contact heat recovery tower to heat the saturating water for the inlet gas saturator, Item 11, and the oxygen saturator, Item 12. The product gas is then ready for the synthesis process.

With respect to capacities, a larger unit located at Oppau operates at substantially atmospheric pressure, has a capacity of $8000m^3$ of coke oven gas per hour, and produces $15000m^3$ of synthesis gas per hour. For $CO + H_2$ operations about 22 volumes of O_2 per 100 volumes of coke oven gas are required. For NH_3 synthesis gas operation about 10 volumes of O_2 per 100 volumes of coke oven gas are supplied, with air used to furnish the remainder of the feed. In either operation the amount of O_2 is varied to control the temperature of the reaction.

Approximate analyses for the inlet and outlet gases are as follows:

	COKE OVEN GAS FEED	CRACKED FOR $N_2 + H_2$	CRACKED FOR $CO + H_2$
CO_2	3%	5%	5%
CO	9%	9%	10%
H_2	55%	48%	80%
N_2	7%	16%	5%
CH_4	25%	0.2%	0.2%

It will be noticed from these data that the partial combustion

process is directed toward the decomposition of the CH_4 in the coke oven gas, covering it into CO and H_2. Thermodynamic equilibrium is said to be substantially obtained.

The carbon formed in the combustion to the extent of 50-200 mg/m^3 outlet gas is removed in the "Schacht" filter. The filter chambers are rectangular, about 3m x 9m in cross section with a bed of 2-8mm particle size coke 5m deep. About 2 liters of coke are removed from the bottom of the bed for each 1000 m^3 of dry gas through the filter. This coke is washed with water to free it of the collected carbon and is then replaced on top of the bed. No attempt has been made to use the carbon washed from the coke, and it is believed to be too coarse for use as carbon black. It is so fine, however, that it gives no trouble by plugging of the catalyst bed or the piping.

The catalyst used in this process is made by saturating 10-22mm particle size magnesite with a Ni(NO3)2 solution to give about 3-4% Ni content by weight in the catalyst. The life of the catalyst is said to be indefinitely long, nevertheless a nickel solution is sprayed on the catalyst bed in sufficiently quantity to add about 1 mg of Ni per m^3 of outlet gas. This addition serves to replace any nickel lost by formation of carbonyl.

The combustion-catalyst chamber unit used in this process is circular in cross section, is lined with silimanite and is in addition insulated to a thickness of about 15 inches. The combustion chamber at Oppau is about 3m in diameter and 3m high, while the catalyst chamber beneath is 3m diameter and 6m high with the catalyst bed 2m deep. It was stated that in commencing operation about eight days are required to bring this unit up to its operating temperature in order to minimize the thermal strains in the masonry.

In the operation of the process the gas composition is controlled primarily with the aid of an infra-red CO recorder and a gravitometer which indicates the amount of N_2 + CO in the exit gas. The operating temperature is controlled by varying the amount of oxygen added to the burner as mentioned above.

A series of experiments carried out at the Bohlen plant by the Lurgi Company in 1941 and 1942 are reported by E. Kapp under the title "Druckspaltung methanhaltiger Gase der Druckvergasung", and a copy of this report is included in the appendix. While the purpose of the investigation was primarily to study the pressure cracking of gases obtained from the Lurgi pressure gas producer (as the name implies) a good general study was also made of the effects of varying several factors influencing the partial combustion process. Only a brief summary and a few comments on these effects are given below. Complete data from the work done are contained in the report.

The combustion chamber originally used in the work described in the above report was designed with an integral preheater, but leakage through the masonry finally forced the abandonment of this idea. Later a regenerative type preheater was designed. The inlet gas used was a mixture which varied slightly in its composition, but the approximate analysis of the gas used in most of the experiments was:

H_2	35.0%
CO_2	32.0%
CO	15.0%
CH_4	1.5%
H_2S	1.4%
C_nH_m	0.9%
N_2	1.4%
O_2	0.2%

In these tests the methane was cracked to about 0.5-4.0%, or a decomposition efficiency of 75-97%, whereas the theoretical equilibrium would be under 0.01% CH_4. The best cracking temperature was found to be 1250-1300°C. In this temperature range the theoretical and actual results were quite close together, as shown by the comparision curves. Simultaneous increase of pressure and throughput improved both the capacity and the cracking. Increase of gas inlet volume without simultaneous pressure increase decreased the available reaction time and reduced the extent of the reaction. It appears that the cracking effect is entirely dependent on this reaction time within the range of capacity of the apparatus, and that in practice, pressure alone did not appreciably alter either the equilibrium or the reaction velocity. Increase in the methane concentration made a higher reaction temperature (about 1400°C.) necessary for the same percent conversion. The quantity of carbon in the outlet gases was appreciably increased as the methane concentration increased. Presence of higher molecular weight hydrocarbons also greatly increased the amount of carbon in the outlet. Higher water content of the inlet gas reduced carbon formation and at the same time increased the usage of inlet gas and of oxygen per m^3 of ideal synthesis gas. Based on this result the water content should be kept as low as possible consistent with control of the carbon formation and of the $CO:H_2$ ratio in the reaction product.

It will be noticed that no hydrogen sulfide was removed in the

cracking but some of the organic sulfur compounds were decomposed, principally to SO_2. This was dissolved and eliminated in the wash water. Incidentally, a small part of this SO_2 sometimes reacted with H_2S to form elementary sulfur which appeared as a white turbidity in the water. The SO_2 in the water has caused some corrosion difficulties with the steel in the piping and equipment.

Later, additional experiments were performed to further investigate the behavior of the sulfur compounds in the combustion and were reported March 17, 1943 in a report entitled "Spaltung von Reingas mit Schwefelbestimmungen". This report is also included in the appendix, and gives more accurate data on sulfur determinations, but the conclusions are about the same.

It was found in both series of tests at Böhlen that the resin-forming compounds that give trouble in the organic sulfur purification step, or "Feinreinigung", and in the subsequent synthesis operations were completely removed by the combustion.

The $CO + H_2$ concentration is approximately constant for any given feed gas at a constant percent conversion. Control of the cracking process to favor one or the other of the three basic reactions will also vary the $CO:H_2$ ratio. This ratio can be still further changed if desirable by inserting a shift reaction converter employing the reaction:

$$CO + H_2O \quad \cdots\cdots\text{---}\cdots\cdots \rightarrow \quad CO_2 + H_2$$
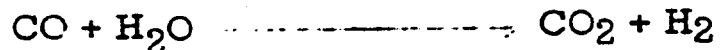
The CO_2 thus produced can be scrubbed out by any suitable process, such as a water wash under pressure. When this methane cracking process is employed to produce gases for the ammonia synthesis, this shift reaction is used to convert the CO into CO_2, yielding additional hydrogen, and the resulting gas is then treated to remove undesirable constituents.

The economy of this methane cracking process depends to a great extent upon the availability of commercially pure oxygen at a low cost. The oxygen for this process is generally made in Germany by the Linde-Franckel low temperature air fractionation process. Since the several Linde-Franckel processes for gas separation are widely used throughout Germany and are covered in other Naval Technical Mission reports the details are not repeated here.

(B) <u>Partial Combustion in a Regenerative Cycle.</u>

In addition to the cracking of methane by partial combustion with

oxygen, H. Koppers GmbH, Essen, developed a straight thermal cracking process employing steam without a catalyst. The process used the absorbed heat of a refractory packed tower maintained above 1200°C. to supply the heat for the reaction. The reaction proceeds according to the following equation: $CH_4 + H_2O \longrightarrow CO + 3H_2$ (-50 cal.). One commercial installation consisting of 3 sets of units installed in 1938-39 was inspected at the "Steinkohlenbergwerk Rheinpreussen Treibstoffwerk" in the Fischer-Tropsch synthetic oil plant near Homberg. It was stated that this was the only installation in Germany using this process, but that others had been built for the Japanese. A simplified flow sheet for this process entitled "Umformungsanlage" showing gas composition, material balance, temperatures, general layout, power consumption, and a rough cost estimate report. In this process the cowper or cracking tower operates on a 16 minute cycle, 8 minutes cracking and 8 minutes heating. The capacity of each cowper unit is about 8,800 normal cubic meters of cracked gas per hour, or about 17,700 normal cubic meters per hour output for a continuous production unit. The temperature in the cracking tower head ranges from 1500°C. at the beginning of the cracking cycle, down to about 1300°C. at the end of the cycle. The cracking tower is completely filled with a special shaped refractory packing, each piece being shaped as follows:

The outside diameter is about 10 inches. The diameter of the center hole in the packing is 4 inches and the sides are also arcs of a 4 inch diameter circle so that the units mesh together to form a geometric pattern of tubes. Each of the pieces is 8 inches high and they are stacked so that the assembled packed tower consists of many refractory tubes of 4 inches diameter extending the full cowper tower height.

When the tower is on the cracking cycle as shown in the equipment on the upper part of the flow sheet (item 6 of the appendix), feed gas is preheated in the gas fired Rekuperator to 100°C., mixed with steam in a ratio 0.85 Kg per normal cubic meter of gas, and is passed through the cowper where it is cracked. The cracked gases then pass through the Brennschacht and the regenerator, leaving this latter unit at about 400°C. They next pass to the tar separator, thence to the precooler washer (leaving at 50°C.), thence to the Theisen water washer, and finally the after-cooler, leaving this last unit at a temperature of 25°C. When the tower is being heated as shown in the lower diagram on the flow sheet, combustion air enters through the regenerator or air preheater, is heated to 1000°C. and is combusted with heating gas in the "Brennschacht" or burning head. The hot gases then pass through the cowper or cracking tower and thence out at a temperature of two hundred fifty to three hundred fifty degrees centigrade.

Inlet and outlet gas compositions are as follows:

	Inlet Coke Oven Gas	Outlet Cracked Gas
CO_2	6.8%	5.1%
C_nH_m	2.5%	-
O_2	0.2%	-
CO	11.5%	19.7%
H_2	46.3%	69.1%
CH_4	24.0%	1.0%
N_2	8.5%	5.1%

A small quantity of carbon black ($30mg/Nm^3$) is also produced but it is not used.

The Koppers methane cracking process is characterized by its bulky equipment, particularly the large mass of refractory packing needed to store and supply the heat for the reaction and to maintain the high temperatures required.

Part II ACETYLENE PRODUCTION BY PARTIAL COMBUSTION

Acetylene is produced in Germany by partial combustion of methane in much the same way as that already described for synthesis gas production. The key difference in the two methods is that in the acetylene production process (a) only relatively pure methane or ethane is used, (b) the gases coming out of the combustion chamber are immediately quenched with a direct water spray, and (c) no catalyst is used.

A special burner is used in order to get the best possible mixing of the feed gas and the oxygen, and thus obtain efficient cracking in the extremely short cracking period. A drawing for such a burner and combustion chamber is shown on Drawing OP 648 - "Acetylenbrenner" in the appendix to this report. In this burner the methane and air enter at the top on opposite sides, flow through separate channels (packed with arranged raschig rings for obtaining homogeneity of the flow), and are mixed at the preheat temperature of about 400°C., at which point reaction begins. Cooling water tubes pass through this initial combustion point, apparently to control the final temperature of the reaction at the desired 1400°C. The reacting

gases then pass down through a thick, perforated tile and are quenched with water immediately below.

A cost estimate entitled "Kostenschatzung für die Gewinnung von 70%igem Acetylen und Synthesegas aus Kohlenwasserstoffen" was prepared in December 1940 by the I. G. Farbenindustrie at Oppau on this process. This report pertains to a unit for the Heydebreck plant, and contains estimated operating costs, estimated construction costs, analyses, heat and material balances, and flowsheets for the process. A copy of the report is contained in the appendix as Item 5.

The two general flowsheets following page 4 of the above estimate show schemes for the process whereby the residual gas after removal of the acetylene is put through another partial combustion to make synthesis gas for ammonia and for Fischer Tropsch processes. This is a customary secondary step with this process.

The recovery of the acetylene is the matter of primary interest. In this process the cracked gas from the burner is compressed to 29 atmospheres and washed with water to remove the acetylene. The absorbed gas is recovered from the water by a three stage expansion. The gas from the first expansion stage is recycled to the compressor and the other two fractions are combined to yield a gas containing 70% acetylene. The third expansion is under vacuum. The lean gas from the absorption is put through the second partial combustion to react the remaining hydrocarbons. Then the gas, now called Cracked Gas II, is passed through a converter to carry out the shift reaction, replacing the CO and H_2O with CO_2 and H_2. When ammonis synthesis gas is produced, the quantities and analyses of the gases based on ethane feed for this process are as follows:

GAS	VOLUME m^3/hr	C_2H_2 %	CO_2 %	CO %	CH_4 %	H_2 %	N_2 %
Ethane Feed	3,070						
Oxygen Feed	3,130						
Cracked Gas I	10,000	9.3	4.0	32.3	6.0	48.4	---
Recycled Gas	446	37.5	15.9	19.5	4.6	22.4	---
C_2H_2 Rich Gas	1,294	70.6	27.7	0.8	0.2	0.7	---
Lean Gas	8,706	0.2	0.5	37.0	6.9	55.5	---
O_2+N_2 Second Combustion	3,738						
Cracked Gas II	11,250	--	3.2	31.2	0.2	42.2	23.2
After Oxidation	14,350	--	24.0	3.0	0.2	54.6	18.2

The flowsheet for the preparation of a hydrocarbon synthesis gas shows the compressor discharge and the water wash at 18 atm instead of 29 atmospheres, and the gas volumes and analyses are as follows:

GAS	VOLUME m^3/hr	C_2H_2 %	CO_2 %	CO %	CH_4 %	H_2 %
Ethane Feed	3,070					
Oxygen Feed	3,130					
Cracked Gas I	10,000	9.3	4.0	32.3	6.0	48.4
Recycled Gas	467	38.5	16.4	18.5	4.5	21.6
C_2H_2 Rich Gas	1,283	70.5	27.9	0.7	0.2	0.6
Lean Gas	8,712	0.2	0.5	37.0	6.9	55.5
O_2 Second Combustion	349					
Cracked Gas II	9,750	--	1.2	38.8	0.3	59.8

Rather than state the operating cost in Reichsmarks (which would have little meaning) figures representing the hourly usage of utilities, labor, etc., which can be used to estimate costs in the United States are given as follows:

	First Combustion	C_2H_2 Concentration	NH_3 Syn Gas Combustion
Ethane, (m^3)	3,070	----	-----
Air, (30 atm, m^3)	---	----	3,350
Oxygen, (m^3)	3,130	----	388
Fuel Gas, $(KCal \times 10^6)$	1.67	----	-----
Elect. Power, (KWH)	120	2,250	-----
Water, (m^3)	160	300	50
Condensate, (m^3)	---	----	2
Labor, (hours)	5	3	3

Computations of operating costs based on these figures will

include repair labor but will not include plant amortization. The major equipment, including 5 burners, was estimated in the report to cost 2,000,000 RM for the 18 atm installation, but these estimates of plant costs are not usually translatable to U. S. practices.

The highest acetylene concentration that has been commercially obtained from this process is about 10%. The usual range is 7% to 9% acetylene. During the course of the interrogation several of the I. G. Farbenindustrie men stated that their partial combustion process for the production of acetylene is definitely more economical than their arc process, unless the cost of electric power is very low.

CONCLUSIONS

Coke oven gas, hydrogenation tail gas, and Fischer Tropsch tail gas were commercially cracked by partial combustion with oxygen or air to produce raw material for several different syntheses. Feed gas consisting of N_2 and H_2 was produced for the ammonia synthesis, and various $CO-H_2$ mixtures were made for use in the methanol, isobutanol, and Fischer-Tropsch syntheses. The Fischer-Tropsch process produced gaseous, liquid and solid hydrocarbons from which gasoline, Diesel oil, lubricants, detergents and a wide variety of chemical products could be obtained.

A variation of the process was also commercially operated for the production of acetylene, which was used for the manufacture of acetone in the particular installation inspected.

W. H. Lyon, Lt. USNR

R. M. Crawford, Technician

GERMAN DOCUMENTS ON METHANE CRACKING BY PARTIAL COMBUSTION

The following documents relating to this subject are transmitted to the Bureau of Ships.

1. I. G. Farbindustrie AG-Ludwigshafen Drawing Op 631 N-Sch 1 dated 17 April 1942 is a flow-sheet for production of synthesis gas by partial combustion of the methane in a coke oven gas mixture.

2. Report dated March 1942 by E. Kapp of Lurgi Gesellschaft Fur Warmetechnik entitled "Druckspaltung Methanhaltiger Gase der Druckvergasung" covers a series of experiments carried out at the Böhlen plant by the Lurgi Company in 1941 and 1942 on the cracking of coke oven gas.

3. Report of March 17, 1943 entitled "Spaltung von Reingas mit Schwefelbestimmungen", covering additional experiments performed to investigate the behavior of the sulfur compounds in the combustion.

4. Drawing number Op 648 titled "Acetylenbrenner" showing a special burner used to get the best possible mixing of the feed gas and oxygen and combust the gas rapidly with water quenching, to yield acetylene.

5. Cost Estimate by the I. G. Farbendustrie "Kostenschatzung für die Gewinnung von 70% igem Acetylen and Synthesegas aus Kohlenwasserstoffen" which contains estimated operating costs, estimated construction costs, analyses, heat and material balances, and flow sheets.

6. Simplified flow sheet "Umformungsanlage" or reforming plant covering the thermal cracking of coke oven gas by the Koppers Process for the production of synthesis gas.

7. Report dated July 13, 1942, by E. Kapp entitled "Berechnung von Regeneratoren für die Druckspaltung".

8.   Report dated July 1, 1931 by Dr. Eckhard entitled "Die graphische Darstellung der aus Sauerstoff, Dampf und Kohlenstoff gewennbaren Mischgase" which presents data on equilibrium of synthesis gas production reactions, including production from methane.

9.   Brief report dated January 10, 1936 from the Oppau Plant to Mitsubishi interests on "Methan-Krackanlage und Winkler Wassergas Generator" giving analyses of gase and utilities demand.

10.   Drawing from Treibstoffiverk Rheinpreussen showing flowsheet and capacity of synthesis gas production by cracking coke oven gas in a generator.

11.   Drawing from Treibstoffwerk Rheinpreussen showing flowsheet of gas cracking plant with analyses and capacities.

12.   Report dated April 17, 1940 from Bohlen entitled "Methan-Spaltung' which contains theory and data on thermal cracking of methane.