I. INTRODUCTION

Previous interrogation of German scientific personnel by numerous investigators and the examination of evacuated documents indicated that further information was desirable on a miscellany of products and processes of interest to the Petroleum Industry. Accordingly, Dr. Pier and a large number of other men of the I.G. Farbenindustrie, A.G. plant at Ludwigshafen/Oppau were further interrogated in July 1945.

The information contained in this report supplements that previously reported in the CIOS report of 16 August, 1945: "Report on Investigations by Fuels and Lubricants Teams at the I. G. Farbenindustrie A.G. works at Ludwigshafen and Oppau", edited by Lt. Col. R. Holroyd (MFP).

II. SYNTHESIS OF HYDROCARBONS FROM WATER GAS MICHAEL PROCESS.

The following information concerning the synthesis of hydrocarbons from water gas was obtained by the interrogation of Dr. Wilhelm Michael who was conducting the research and development on the so-called "Michael Process". Two methods of operation had been studied that were outlined briefly in the earlier report on Ludwigshafen.

Both methods employed an iron catalyst which was stated to have the following advantages over the cobalt catalyst:

a. The gasoline is better.

b. A higher concentration of olefins is formed.

c. The process is cheaper.

Dr. Michael had also investigated the use of iron catalysts in a tubular reactor at reduced temperatures.

Special precautions are required with the iron catalyst, which more than the cobalt catalyst, is subject to "run-away" reaction and the formation of carbon on the catalyst. The methods investigated were designed to prevent the conditions which lead to carbon formation.

A. Fixed-Bed Circulating-Gas Process

In this process gas is recirculated over the catalyst and through a cooler at such a rate that the temperature rise in the catalyst bed is limited to a maximum of 10°C. The reaction is carried out at a pressure 20 atmospheres. At lower pressures the reaction velocity is too small. The gas recycle ratio is 100 volumes of recycle to one volume of fresh gas. Contact time in the catalyst bed is approximately one half to one second per pass, with a gas velocity of about 1 m. per second. The flow sketch (Fig.I) illustrates the process. An important limitation is that the gas must flow through the catalyst bed without turbulence, otherwise static zones form and lead to a dangerous temperature rise resulting in the formation of methane and carbon. This necessary flow condition has been obtained in small-scale experiments (as shown in Fig.1), using a 5 liter catalyst bed which were conducted successfully for as long as 10 months. Experiments of shorter duration have been successful in the same type of system with a 400 liter catalyst bed. Dr. Michael believes this single-bed design could be built to still greater diameter; channeling is the limitation.

With larger scale experiments (4-cubic meter catalyst bed), space restrictions required the bed construction shown in Fig. 2. The operation of this unit was unsuccessful, because the gas undergoes a change of direction simultaneously with a velocity change (owing to change in diameter), which results in turbulent flow and stagnant spots develop in the catalyst bed. This unit was shut down after 2 months of operation because of the formation of carbon pockets. A further large-scale experiment utilizing cylindrical construction was proposed but the equipment was not built, due to the war. This unit was to have alternating sections of catalyst and condensers, in one container, as shown in Fig. 3

Reaction Data

Gas	CO: H_2 about 1:1 or 4:5
Pressure	20 atm.
Gas purity	Sulphur - under 2 mg. per cu.m., CO_2 free.
Gas recirculation	100 times.
Temperature change of gas	10°C.
Working temperature	300-325°C. (mainly 325°C.)
Catalyst	Sintered iron catalyst. Pellets about 1 cm.
CO_2 in exit gas	40-45%

Output per cu.m. of catalyst: 700-800 kg./day.

Catalyst

The best gasoline is obtained with iron catalysts when the synthesis is conducted above 300°C. Therefore it is necessary that the catalyst be insensitive to such temperatures and a good conductor of heat. This type of catalyst is obtained by high-temperature sintering of iron powder pasted with about 1% of alkali during the reduction with hydrogen. An example of the catalyst preparation is as follows: Fine iron powder prepared by thermal decomposition of iron carbonyl is pasted with a concentrated solution of borax (1 gram of borax per 100 grams of iron) and formed into approximately 1 cm. cubes. In order to insure loose packing, the cubes are made with slightly irregular edge lengths. The cubes are sintered and reduced with hydrogen at 800-850°C. for 4 hours. The catalyst is cooled in a hydrogen atmosphere, which is replaced by carbon dioxide before charging to

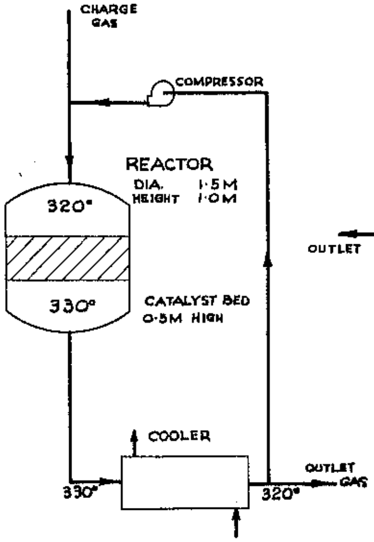

FIG. 1

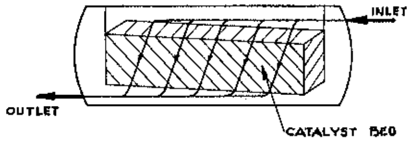

FIG. 2

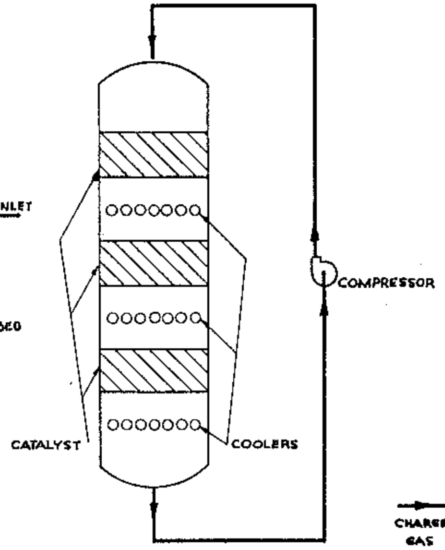

FIG. 3

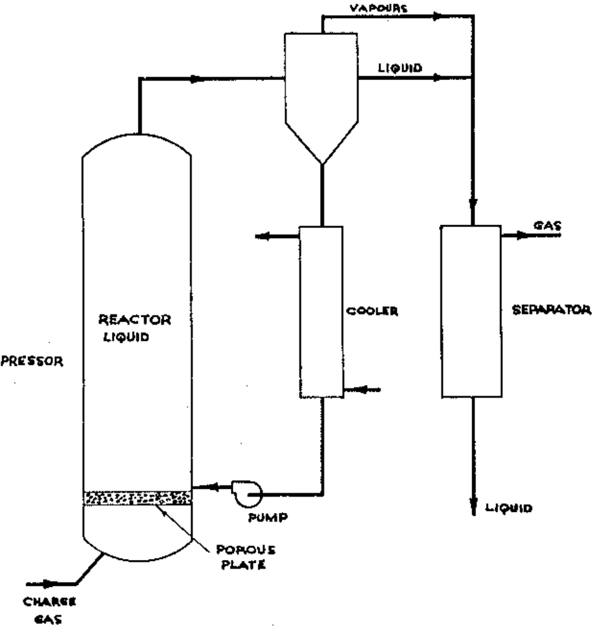

FIG. 4

SKETCHES FROM DR. MICHAEL
I.G. LUDWIGSHAFEN OPPAU
31ST JULY 1945

the reactor. In place of iron powder, Fe_2O_3 may be used in the preparation but it yields a catalyst which is very porous and of relatively low stability.

Reaction:

In contrast to the cobalt catalyst which yields, besides hydrocarbons, mainly water, the iron catalyst forms predominantly carbon dioxide. Under the conditions given above, 80-85% gas conversion is obtained with 40-45% of carbon dioxide in the exit gas. If a two-stage process is employed, this carbon dioxide must be removed. Condensation takes place in 3 cooling stages as follows:

1) Cooling to 120°C to condense the paraffin and some of the water;

2) Cooling to 20°C to condense the gas oil, heavy naphtha and additional water:

3) Cooling to minus 40°C to condense light gasoline and part of the liquifiable hydrocarbon gases. Prior to this stage the gas must be intensively dried with calcium chloride or silica gel.

The exit gas from this third cooling stage is washed free from carbon dioxide with water or alkazid solution and is further converted in a smaller second system, whereby an overall conversion of 92 to 95% is obtained. The products from this second system are separated in a manner similar to that described above.

Composition of Product.

When operating with a hydrogen to carbon monoxide ratio in the charge gas of 5:4, the exit gas from the first stage is as follows:

CO_2	40-45%
H_2	25-30%
CH_4	5-10%
CO	15-20%

The so-called "useful" products are as follows:

$C_2 - C_4$ (excluding ethene)	30%	
Ethylene	8%	
Propylene	9%	
Propane	3%	
Butylene	8%	3/4 of iso-structure
Butane	2%	

Gasoline (to 200°C.)	48%	(7% alcohol content)
Gas oil	14%	(4% " ")
Paraffin	1%	
Alcohol (in aqueous layer)	7%	(mainly C_2)

Only straight-chain and alpha methyl primary alcohols are produced. For every 100 kg. of these useful products, 25 kg. of methane and ethane are formed. From the liquefied hydrocarbon gases, additional gasoline can be prepared by polymerization and alkylation.

The crude gasoline product has an octane number of 68 to 70 (research method). By passing this crude product over alumina at 400-450°C. for the removal of oxygen and then refining over fuller's earth at 180-200°C, the octane number is increased to 84 (research method) and to 75-78 by motor method. The refining loss is about 5%. The gasoline, which has an olefin content of about 70%, must be inhibited for storage. The gas oil has a cetane number of 45 to 50.

Oxygenated Products in the Water.

Acetaldehyde	5%
Acetone	10%
Ethenol	55%
Propanol	20%
Butanol and over	10%

B. The Foam Process

If the object of the operation is not to produce a gasoline, but rather chemical products, olefins of greater chain length, such as occur in the gas-oil fraction, are the more desirable compounds. To increase the gas-oil yield, the operating temperature must be lowered (250° or below). Therefore, to obtain a reaction, a more active catalyst than the sintered catalyst is required. The following process was developed to work with the highly active catalyst in a liquid phase in which the reaction gases are only slightly soluble and in which the catalyst is suspended in a finely divided state. Fig. 4 shows the flows.

Apparatus.

The gas distribution is best effected by ceramic plates (0.15 mm. pore size). The finely divided catalyst is kept in suspension in the oil in the reactor by the ascending gas stream. The high-boiling part of the reaction product serves as the suspending medium (250-300 kg. of iron per cu.m. of oil). The gas passes out overhead through a separator. The liquid is slowly carried upward and flows overhead into the separator. The spent gas and the admixed vaporized product pass to the condensers. From the separator, only the excess liquid is removed. The recycle suspension passes into a cooler, and thence to a pump, which returns it to the reactor. At a cir-

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culation temperature of 250° C, the suspension temperature increases 10°C over the period of 3 minutes in the reactor.

After the separation of the product as described in section A. further conversion of the gas is possible by recirculation (after removal of CO_2). Several stages are preferred, since in a second stage 85% conversion is reached and in a third, 90%.

Reaction Data.

Gas	-	$CO:H_2$ about 1:1 or 4:5
Pressure	-	20 atms.
Temperature	-	about 250°C.
Reaction duration	-	about 3 minutes/cycle
Temperature rise	-	10°C.
Conversion	-	70%
CO_2 in exit gas	-	40-45%
Yield	-	1 cu.m. reaction volume yields 350-450 kg./day.

Catalyst

In contrast to the sintered catalyst, the reduction of the catalyst for the "Foam" process is effected at lower temperature (350-450°C) with a very high hydrogen throughput. Iron oxide is obtained in the finely divided state either by precipitation or by the decomposition of iron carbonyl. The oxide is stirred into a paste with Alkali solution (K_2CO_3 or potassium borate) and formed into small granules which are dried, reduced and ground fine in a ball mill in admixture with gas oil.

The iron carbonyl can also be decomposed in the suspension oil, in which case, a smaller amount of iron suffices.

Product

Liquefiable gas (C_3 and C_4)	10%
Gasoline < 200°C	40-50% with 70% olefins.
Gas oil < 350°C	30% with 40-50% olefins.
Paraffin	20-25%, of which 2/3 boil over 450°C.

For 100 Kg. of utilisable product, there are 5-10 kg. of CH_4.

Utilization of Product.

The olefins are readily polymerised to lubricating oil or converted to sulphonates (detergents) with sulphuric acid. By reaction with $CO-H_2$, the olefins may be converted into higher alcohols, aldehydes or acids.

Large-Scale Experiment.

The largest unit, tried out was a 1½ cu.m. system (including the separator). It produced 450-500 kg. of product per day. After two months a catalyst deposit was observed in the upper portion of the reactor. A stirrer was added to prevent this occurrence, but so much deposit formed around the stirrer and then fell off that the foam-plate was covered.

The final solution of these problems was prevented by the war.

C. Iron Catalyst in Tubular Reactors.

Dr. Michael also gave the following information on iron Fischer-Tropsch catalysts.

Synthesis iron catalysts produced by precipitation in the same manner as the cobalt catalyst, is unsatisfactory because a "run-away" reaction develops: a sudden temperature rise occurs, in which the formation of methane and carbon predominates. The catalyst preparation was changed, therefore, in order to obtain a solid catalyst with good heat conductivity and high activity. In this method the sintering was carried out before the reduction and the reduction itself performed at as low a temperature as possible while maintaining a high hydrogen velocity.

In order to attain high activity, 5-25% of alkali-earth metal in the form of oxide or carbonate, (MgO or $MgCO_3$ preferably) is incorporated into the catalyst. The iron oxide or hydroxide is mixed with the alkali earth and 1-2% of K_2CO_3 or $K_2B_4O_7$, pressed into pellets, heated to 850°C, and then reduced with hydrogen after cooling to 350-450°C. The catalyst has a very high activity at 240°C and lower temperatures, and excellent thermal stability in the tube reactor. The catalyst was used in a 20-liter tube reactor for several months under the following conditions:

Pressure, atm.	20
Temperature, °C	230-250
Charge-gas composition	$CO:H_2$ = 4:5 to 5:4
Conversion	70-80%

Under the above conditions the yield was 0.35 - 0.45 kg. per liter of catalyst per day of the following products:

Liquefiable gas (C_3, C_4)	10%	with 70% olefins
gasoline (<200°C:)	35-50%	" 70% "
gas oil (<350°C:)	25-35%	" 40-50% "
Paraffin wax:	15-25%, (60% boiling above 450°C.)	

The oxygen content of the gasoline was 4-6%
The oxygen content of the gas oil was 3-5%

The methane yield was about 10 kg. per 100 kg. of the above products.