Additional Information Concerning the Fischer-Tropsch Process and its Products

Introduction.

In March, April and May of 1945 the Fischer-Tropsch plants and research institutions were investigated by joint British-American teams sponsored by the Ministry of Fuel and Power and the U.S. Technical and Industrial Intelligence Committee. In the course of these investigations a very large number of documents relating to the Fischer-Tropsch process were collected and brought back to London for detailed study. As a result of this study and from an examination of the Field Team Reports of the original and subsequent investigations, it was found that there still existed a number of gaps in our information concerning the operation and development of this process in Germany. There was a lack of detailed cost information for the operation of the process at the more efficient plants, and many of the important details of plant operation and of the research work on iron catalysts were either missing or inadequately reported. Further information was required concerning the refining and properties of the waxes produced in the process and on certain aspects of the production of synthetic fatty acids and detergents from the primary products.

The information reported herein was obtained as a result of investigations carried out with the object of making good these deficiencies.

In many cases information on the same point was sought from several targets, but as all the targets have been previously assessed and there is not therefore any interest in the targets per se, this Report has been written on a subject basis.

Documents which were obtained in the course of the investigations are listed and described at the end of this Report. The small numbers in the text refer to these documents.

Production of Synthesis Gas

On being asked about the various processes actually in use, or proposed, for the production of synthesis gas, Ruhrchemie said that they could give no better general account than that already published by A. Thau in Oel and Kohle, 1942, p. 589-765. This has to do with the technical aspects. The costs of preparing synthesis gas by these processes are compared in Brückner's 'Handbuch der Gasindustrie' Vol. II Part II p. 58 (1940), the data being taken from papers by W. Schultes, Glückauf, 1936, 72, 273 and F. Martin, Chem. Fabrik, 1939, 12, 233.

All the synthesis plants in Western Germany obtained their synthesis gas by mixing water-gas with a gas richer in hydrogen obtained either by cracking coke-oven gas or by subjecting water-gas to the water-gas shift reaction to give the so-called converted water-gas. More details on these processes were therefore available.

Water-Gas Generation.

The water-gas plant of Ruhrchemie was the first plant constructed by Demag and it gave a great deal of trouble on account of corrosion in the stack, which was unlined. This was not limited to Ruhrchemie, because the Koppers water-gas plant built for Rheinpreussen worked so badly that a new plant had to be installed free of charge by the makers under the terms of the guarantee. Again the trouble was due to corrosion in the stack which had to be lined in the newer generators. At the moment Rheinpreussen consider the Demag generators are better than their own Koppers generators.

Even when the water-gas plant is running well, it is essential to have a uniform supply of coke if a constant supply of gas of constant composition is to be obtained. Ruhrchemie were particularly badly placed in this respect as they obtained their coke from five different firms. Essener Steinkohle, on the other hand, were ideally placed, because the mine, the coke-ovens and the synthesis plant were on the same site and under the same management. The synthesis plant was, in fact, specially built to absorb the coke produced as it was not very suitable for metallurgical purposes.

The efficient working of the generator plant is the most important step in the whole synthesis process from the point of view of thermal efficiency, and the much better thermal efficiency of Essener Steinkohle as compared with Ruhrchemie is largely due to this factor. Thus, for example, Ruhrchemie employed 100 men for running repairs on the generator plant whereas Essener Steinkohle only needed 30. For efficient working adequate reserve is necessary, and although Essener Steinkohle had eleven generators, ten in use and one in reserve, they would have preferred twelve, ten in use, one in reserve and one being repaired.

The steam consumption by the water-gas plant is by no means constant, and in the case of Essener Steinkohle, this accounts for the item in the cost statement in Table 26, showing steam taken from the colliery, although there are items in the same statement for steam sold to the colliery.

The detailed costs for the production of water-gas by Ruhrchemie in 1943-4 are given in Table 1, and a comparison of the data given there with the corresponding English costs should be useful in converting other German synthesis costs for the same period, as given in this report, into present-day English costs. The table does not include capital charges, but these can be estimated from the capital costs of the various items of the plant concerned which are as follows:-

	RM
East Generator Plant	3,067,946
Machine Shop for Water-gas Plant	427,087
West Generator Plant	4,147,211
Ash Disposal Plant	134,701
Water-gas Holder, 20,000 cu.m.	358,300
Settling Pools	98,587
Cooling Plant	264,909

Table 1. Costs for Production of Water-Gas (Ruhrchemie)

Working Costs for 1943-4 for the production of 470,719,220 cu.m. water-gas

	Quantities		Price	Costs	
	Total	Per cu.m.	RM	Total, RM	Per cu.m., Rpfg.
Input					
Coke	344,262 t.	0.731 kg.	22.80/t.	7,864,148	1,671
Transport of the Coke			0.60	199,150	0.042
			23.40	8,063,298	1.713
Working Costs					
Wages				278,280	0.059
Salaries				50,409	0.011
				328,695	0.070
Energy					
Electric Power	5,181,370 kwh.	0.01 kwh.	0.018/kwh.	89,913	0.019
Steam	658,182 t.	1.40 kg.	2.105/t.	1,381,807	0.293
Fresh Water	446,597 cu.m.		0.067/cu.m	29,841	0.006
Feed Water	1,148,479 cu.m.		0.232/cu.m	266,217	0.057
Reflux Cooling				7,021	0.002
				1,774,801	0.377
Various Materials				168,174	0.036
Repairs and Maintenance				1,208,465	0.257
Other Costs (Transportation of Ash etc.)				78,145	0.016
Insurance and Dues				8,681	0.002
Laboratory				45,968	0.010
General working costs				156,327	0.033
Total Working costs				3,769,258	0.801
Total Input & Working Costs				11,832,557	2.514
Credit for Steam	650,184 t.			1,363,796	0.290
Total				10,468,758	2.224

The Production of Cracked Coke-Oven Gas.

Rheinpreussen prepared their synthesis gas both by adding cracked coke-oven gas to water-gas, and by making the adjustment in composition with converted water-gas. They say that the former method is the better one, on economic grounds. They also say that in general it is better to perform the cracking in a separate unit and not in the generator, for two reasons. Firstly, because the temperature in the generator is not high enough to cause complete cracking of the methane. Thus only some 60% of the methane is cracked at 1200°C. and a temperature of 1300°C. is necessary to crack 95%. If the generator is worked at a rather higher temperature than normal so as to get sufficient cracking of the methane, the costs increase as the lining of the generator disintegrates quicker and re-lining has to be done more frequently. The second reason is that undesirable resin-forming constituents of the coke-oven gas will pass through the generator at 1200°C. unchanged, while they are completely destroyed at 1300°C. in an external cracking unit. For these reasons Rheinpreussen changed over from internal to external cracking.

Conditions at the Essener Steinkohle plant were rather exceptional, as a result of which that company found it better to crack in the generator at 1100 - 1200°C. in spite of the above considerations. Being a new plant of good design, their coke-oven installation gave a gas containing an abnormally high proportion of hydrogen (see Table 14) so that a very complete cracking of the methane is unnecessary and in practice only some 40 - 50% of it was cracked. Moreover, they prefer to leave some methane as diluent in the synthesis gas, because then the residual gas from the synthesis can be sold very profitably as town's gas on account of its high methane content (see credit items in Table 26). As far as they know, this methane has no effect on the synthesis.

For costs of making synthesis gas from water-gas and cracked coke-oven gas, see Table 26.

Water-Gas Conversion.

Ruhrchemie prepared their synthesis gas from water-gas in this way, and the following information was supplied by them about the process. They originally thought that their process for the purification of the gas from organic sulphur compounds would be unfavourably affected by gas rich in carbon monoxide, and they mixed the converted water-gas with the main stream of water-gas before passage through the above mentioned purification system. This was found to be unsatisfactory, however, as there was incomplete mixing of the converted gas and the water-gas, the two passing down a wide pipeline in two separate streams. Thus one or other of the purification units could be exposed to converted gas only and as this contained no oxygen - the oxygen originally added being used up in the conversion step - the purification was unsatisfactory.

As a result, they re-examined the whole position, found that the purification system for the removal of organic sulphur compounds worked perfectly well with water-gas, and hence they passed all the water-gas through it before branching off a fraction for conversion by the water-gas shift reaction.

Various catalysts were used for the conversion but the brown oxide catalyst supplied by the I.G. Farben consisting of a mixture of iron oxide and chromium oxide, was the usual one. The catalyst was arranged in a reactor of 3.2 m. diameter, in four layers, each 750 mm. high. The reactor contained 26 - 28 t. catalyst. A heat exchanger with 1400 sq.m. surface was built beneath the reactor and the height of the combined unit was 14.5 m. The water-gas was first saturated at 70°C. in a tower 2.40 m. diameter and 27 m. high, using the water from the cooler placed after the reactor. A steam injector, using steam at 9 atm., was used to supply the requisite water vapour for the reaction and to pass the gas forward into the heat exchanger. The converted gas, on leaving the reactor, was passed through a cooler, of 3.10 m. diameter, 27 m. high, filled with five layers of Raschig rings, and finally passed out of the plant at 25 - 30°C. Both in the cooler and in the saturation tower hydrogen sulphide is liable to be formed by the action of bacteria on calcium sulphate in the water, and since the converted water-gas does not pass through any purification plant before reaching the synthesis catalyst, this formation of hydrogen sulphide must be suppressed. This was done by keeping the water free from sulphate by recirculating it through a separate cooling tower. If for any reason this recirculation was interrupted, the bacteria were controlled by adding a little zinc chloride to the water.

For the catalyst employed, the water-gas shift reaction starts at 370°C., but the temperature actually used was from 420 to 480°C. After the second layer of catalyst, condensate water, free from residues, was sprayed in to control the temperature, the reaction being exothermic, and to save steam. The necessary excess of steam increases with the temperature.

If no spraying were done at this stage and if the incoming water-gas were not saturated with water vapour, the steam consumption was 0.8 - 1.0 kg./cu.m. water-gas, whereas by working the process as described this was reduced to 0.6 - 0.7 kg./cu.m. The spraying must not be done, however, if condensate water containing less than 2 - 5 mg./litre is not available, because otherwise the catalyst rapidly becomes choked with scale from the water.

When a new charge of catalyst is brought into use, it is first heated to 370 - 400°C. with hot flue gases and then the water-gas and steam admitted. Reduction occurs and after a few hours the catalyst works normally. If the reaction on this catalyst had to be interrupted for any length of time it was found best to oxidize it with a mixture of nitrogen and air, or if this were not available, steam and air, before restarting. During use the the catalyst slowly disintegrated and after two years had to be taken out and sieved. After recharging it lasted another 1 - 2 years.

Each unit, as described, converts 6,000 N.cu.m. water-gas/hour, and Ruhrchemie had five such reactors, two saturation towers, and three coolers (2 in use, 1 in reserve). The plant was built by Bamag-Meguin A.G., Berlin. Its performance can be judged by the following data for the year 1943-4:-

The water-gas plant produced 59,000 cu.m./h. and after purification 16,000 cu.m./h. of this gas was taken out of the main stream and passed through the water-gas conversion plant, which yielded 21,100 cu.m./h. converted gas. Part of this was compressed, passed through a plant for washing out carbon dioxide, and mixed with compressed purified water-gas to give synthesis gas for the medium pressure synthesis. The remainder was mixed with the unconverted water-gas to give synthesis gas for the atmospheric pressure synthesis. Analyses at the various steps are shown in Table 2.

The cost of the water-gas conversion was 0.20 Rpfg./cu.m. synthesis gas, exclusive of capital charges.

Table 2.

Preparation of Synthesis Gas, Ruhrchemie 1943-4.

	Water-Gas	Converted Water-gas (before plant for removal of CO_2)	Converted Water-gas (after plant for removal of CO_2)	Synthesis Gas	
				Medium Pressure	Atmospheric Pressure
	%	%	%	%	%
CO_2	6.0	29.2	8.9	7.0	14.4
CO	39.2	4.7	7.6	34.5	26.7
H_2	49.1	61.2	77.2	52.7	53.2
CH_4	0.4	0.4	0.4	0.4	0.4
N_2	5.3	4.5	5.9	5.3	5.3

Production of Synthesis Gas Directly from Brown Coal.

Brabag had one Didier plant of capacity 35,000 cu.m./h. and seven Koppers plants, each of capacity 30,000 cu.m./h. Both gasified brown coal briquettes, but in addition to this fuel, coke was also required to make producer gas for underfiring the Koppers plant.

The Didier plant was not very satisfactory because the brick chambers always tended to leak, but it served as a good standby when the Koppers plant was out of order. The gas produced in it was more expensive than the Koppers gas and contained four times as much condensate.

The Koppers plant was the main source of gas, which it produced at about 0.7 - 0.8 Rpfg./cu.m. The chief trouble was that the brown coal briquettes disintegrated in the generator if they contained too much moisture, and so formed dust which blocked the slots through which the gas left the generator, in this way stopping the gas production from that generator completely. This could be avoided by altering the position of these slots and increasing the size of the top of the generator, but it was too expensive to alter the existing generators in this way. In the middle of 1943 Brabag specified that the brown coal should only contain 5 - 15% moisture before briguetting and in this way the dust trouble was avoided, but the price of the briquettes was increased from 9 to 12 RM/t.

Lurgi Pressure Gasification.

The production of synthesis gas from brown coal by this process has already been described in detail elsewhere and the only new fact brought to light was that little progress had been made during the war years with the newer method in which the ash is withdrawn in the liquid state.

A statement by Lurgi of much greater interest from an English point of view was that they had prepared synthesis gas directly from bituminous coal and anthracite by their process, full scale trials lasting several weeks having been carried out. The data given in Table 3 are based on the trials with bituminous coal, and the calculations were made for a plant to produce 132,000 N.cu.m. synthesis gas/hour, which would be required for a synthesis plant to produce 150,000 t. products/year.

In considering the results given, the figure of 4% given for the methane in the gas is too low, and for large works practice it might well be 6 - 7%, because the control of the individual generators would then be less accurate. This extra methane is really no disadvantage as it makes the residual gas from the synthesis more valuable as town's gas (see p. 5). If it is desired, the methane can be cracked in the generator by working at a rather higher temperature, but then as much oxygen is needed as for the Winkler generator.

Table 3.

Synthesis Gas from Bituminous Coal by the Lurgi Process.

I. Technical Data.

1. Composition of the Coal:

Size	2 - 30 mm.
Tar	1%
Ash	4%
Volatile Matter	10%
Gross Calorific Value	8100 kg.-cal./kg.

2. Composition of the Synthesis Gas:

CO_2	1.0%
O_2	0.1
CO	31.4
H_2	62.0
CH_4	4.0
N_2	1.5
Inert-free Gas	93.4
Gross Calorific Value	3220 kg.-cal./kg.

3. Production Data and Materials Used:

a)	Gas Production	132,000 N.cu.m./h.
b)	Coal used	520,000t./year = 62.0 t./h.
c)	Oxygen used	0.19 N.cu.m. pure O_2 /N.cu.m. synthesis gas = 25,100 N.cu.m./h.
d)	Steam	1.1 kg./N.cu.m. synthesis gas
	for Gasification	145 t./h.
	for Heating	10 "
		155 "

e) Energy for

Gas Production	200 kw.
Charging the coal	70 "
Cooling-water pumps	370 "
Air compressors	10,300 "
Oxygen Compression	2,940 "
High Pressure Air Compression	1,100 "
Ammonia compression	120 "
Cooling-water pumps	120 "
Other machines, and lighting	180 "
Pressure water pumps	8,500 "
(in the event of failure of a water turbine)	9,600 "
Supply of air	800 "

f) Cooling Water

Cooled water for gas cooling	2,400 cu.m./h.
for O_2 plant	1,200 "
Fresh water	180 "

g) Effluent water	96 "

4. <u>Amount of Plant:</u>

a) Oxygen Plant

Air turbo-compressors	3 in use 1 in reserve
Oxygen turbo-compressors	3 in use 1 in reserve
Separating Plant	7 in use 1 in reserve

b) Gasification

Gas Generators	22 in use 2 in reserve
Cooler	10 in use
Superheaters	4 in use

c) Pressure Water Washers

Pressure Washing Towers	20 in use
Pumps	4 in use
Turbines	4 in use
Aeration Towers	4 in use

5. **Personnel:**

Manager	1	
Engineers	2	
Foremen	4	
Laboratory Assistants	4	
Fitters		
Gasification Plant		4 x 2 = 8
Oxygen Plant		4 x 4 = 16
Pressure Water Washer		4 x 2 = 8
Labourers		
Gasification Plant		4 x 12 = 48
Oxygen Plant		4 x 4 = 16
Pressure Water Washer		4 x 4 = 16
General		4 x 5 = 20

6. **Price of Raw Materials:**

Coal (in the bunkers)	14 RM/t.
Fresh Water	6 Rpfg./cu.m.
Purification of Effluent	0.50 RM/cu.m.

	a) Without Washing	b) With Pressure Water Washing
Steam, 80 atm.	2 RM/t.	2RM/t.
Electric Power	2 Rpfg./kwh.	2 Rpfg./kwh.

7. **Wages and Salaries:**

	RM	RM
Management (a proportional amount)	25,000	30,000
Engineers "	10,000	12,000
Laboratory Assistants "	9,000	10,000
Fitters	72,000	96,000
Labourers	184,800	220,000
	313,800	384,000

II. **Cost of Construction of the Whole Plant.**

16,882,000	20,198,000

III. Working Costs.

		RM	RM
a)	Coal 520,000 t.	7,280,000	7,280,000
b)	Cooling-Water 180 x 8,400 cu.m.	91,000	91,000
c)	Purification of Effluent 96 x 8,400 cu.m.	403,000	403,000
d)	Materials and Repairs, without wages, 3.5% of capital cost	590,000	590,000
e)	Wages and Salaries	334,000	404,000
f)	Capital Charges Amortization, 9% of capital cost	1,520,000	1,816,000
	Interest, 5% of capital cost	845,000	1,010,000
g)	Steam 155 x 8,400 t.	2,600,000	2,600,000
h)	Electric Power 2,380 x 8,400 kwh.	400,000	
	13,180 x 8,400 kwh.		2,215,000
		14,063,000	16,525,000
	Credit for Methane	836,000	836,000
		13,227,000	15,689,000

IV. Gas Production Costs.

A) Without Cracking Residual Gas.

a) Production costs for 1 N.cu.m. synthesis gas, compressed to 9 atm., but without the cost of removal of CO_2:

1.2 Rpfg./N.cu.m.

b) As above, but including the CO_2 removal:
1.41 Rpfg./N.cu.m.

c) As above, but with the compression costs of 0.25 Rpfg./N.cu.m. deducted:
1.16 Rpfg./N.cu.m.

B) <u>With Cracking of Residual Gas.</u>

a) Without removal of CO_2:

	RM
Working Costs for Cracking	816,000
Compression of Cracked Gas	866,000
Working costs for Gasification Plant	14,063,000
	15,745,000

Production Costs for
Synthesis Gas compressed to 9 atm.
<u>1.08 Rpfg./N.cu.m.</u>

b) With removal of CO_2:

Working Costs for Cracking	816,000
Compression of Cracked Gas	866,000
Working Costs for Gasification Plant	16,525,000
	18,207,000

Production Costs for
Synthesis Gas compressed to 9 atm.
<u>1.25 Rpfg./N.cu.m.</u>

c) Production Costs for
Synthesis Gas, without compression:
<u>1.00 Rpfg./N.cu.m.</u>