TABLE XLVIII

UTILITY CONSUMPTIONS IN ALKYLATE MANUFACTURE

Operation	HP steam 12·5–15·5ats te/te alkylate	LP steam 2·6ats te/te alkylate	Electric power kwh/te alkylate	Circulating water m³/te · alkylate	Fuel gas te.cal/te alkylate
Dehydrogenation	—	1·27	98	24	2,000
Compression of dehydrogenated gas and absorption unit	0·14	—	216	84	—
Alkylation, including refrigeration ..	4·88	—	72	128	—
Butane-isobutane separation and depropaniser	—	4·4	24	128	—
Debutanising of alkylate, and alkylate distillation	1·20	1·53	186	128	—

TABLE XLIX

COMPOSITIONS OF CATALYSTS USED ON THE INDUSTRIAL SCALE

Code number	Use	Analysis
(Methane steam)	H_2 + CO from hydrocarbons	25% Ni_2O_3, 14% MgO, 28% cement, 33% kaolin
(Brown oxide)	CO conversion	85% Fe_2O_3, 15% Cr_2O_3
—	Methanisation of H_2 + CO	61% Ni, 9% MgO, 30% kieselguhr
10927	Hydrogenation of tar, pitch and petroleum residuum	5% Fe on "grude" (Winkler coke from brown coal)
Bayermasse	Brown coal hydrogenation	Crude hydrated iron oxide (by-product of aluminium industry)
—	300ats bituminous coal hydrogenation	0·07% stannous oxalate + 1·0% NH_4Cl, on dry coal fed
—	700ats bituminous coal hydrogenation	1·2% $FeSO_4 7H_2O$, 1·5% Bayermasse, 0·3% Na_2S, on dry coal fed
5058	Vapour phase presaturation, also MTH and TTH processes	100% WS_2
7846	Early 5058 substitute	10% WS_2, 3% Ni_2O_3, 87% Al_2O_3
8376	Final 5058 substitute	25% WS_2, 3% NiS, 72% activated Al_2O_3
6434	Vapour phase splitting	10% WS_2 on activated Terrana earth
—	Welheim 700ats splitting	0·6% Mo, 2% Cr, 5% Zn on activated Terrana, sulphided to 5% S
7360	DHD	⎫
5436	Hydroforming	⎬ 10–12% MoO_3 on Al_2O_3
5931	Hydroforming	⎭
7935	Improved DHD	15% MoO_3 on activated Al_2O_3
5939	Hydroforming	5% MoO_3 on activated Al_2O_3
5635	Hydroforming	5% MoO_3 on technical Al_2O_3, with up to 0·7% Na_2O
6448	Butane dehydrogenation	8% Cr_2O_3, 2% K_2O, 90% Al_2O_3
4821	Butylene polymerisation	75% P_2O_5, 4–5% H_2O on asbestos
—	Butylene polymerisation	65% P_2O_5, 26·75% H_3PO_4, 1·23% H_2O, 11·09% MgO, 6·45% SiO_2, 0·71% CaO, 0·30% Al_2O_3, 0·28% Fe_2O_3, 0·09% Na_2O, 0·1% SO_3
5615	⎫	⎧ 2WS_2.NiS
6718	⎬ Iso-octene saturation	⎨ 2WS_2.NiS
3076	⎭	⎩ WS_2.2NiS
1132	Isobutanol synthesis	33% Cr_2O_3, 60% ZnO, 1% K_2O, 1% graphite, 5% H_2O
5780	Isobutanol dehydration	γ-Al_2O_3, with 0·03–0·04% Na_2O, 4% H_2O
2730	Isobutylene polymerisation	35% H_3PO_4, 5% H_2O on activated C
—	Organic S removal	70% Luxmasse, 30% Na_2CO_3
—	Fischer catalyst	31·9% Co, 1·6% ThO_2, 2·6% MgO, 63·9% kieselguhr

D—Fischer-Tropsch Process

1. INTRODUCTION

The process usually associated with the names of Fischer and Tropsch, the discoverers of the basic reaction, comprises the synthesis of liquid and solid aliphatic hydrocarbons from mixtures of carbon monoxide and hydrogen. The object of the present Section is to give an account of the industrial operation of this process in Germany together with a summary of the research and development work which was carried out in this field during the war.

i. HISTORY OF THE PROCESS

In 1925, F. Fischer and H. Tropsch, of the Kaiser Wilhelm Institut für Kohlenforschung, Mülheim, Ruhr, published an account of their synthesis of a mixture of liquid and solid aliphatic hydrocarbons from water gas at temperatures in the region of 200°C at atmospheric pressure in the presence of catalysts based on iron, cobalt or nickel. The synthetic oil consisted almost entirely of straight-chain paraffin and olefine hydrocarbons and somewhat resembled a paraffin-base

petroleum. Research on the process continued at the Institute, more active catalysts were developed and the commercial possibilities of the process became apparent to the Ruhr coal owners who were concerned to find outlets for their surplus coke. Accordingly the Ruhrchemie AG (a company founded by the Ruhr coal syndicate) who had a synthetic ammonia and nitric acid plant at Oberhausen-Holten, were appointed licensees for the development of the Fischer-Tropsch and allied processes.

Following the development work by Ruhrchemie, construction of the first commercial unit was started in 1935 and completed in 1936. By 1939 a total of nine Fischer-Tropsch plants had been erected in Germany under licence from Ruhrchemie with an aggregate rated output of 740,000te/yr synthetic oil. The first plants to be erected were designed for operation at atmospheric pressure, but as a result of research work both at the Kaiser Wilhelm Institute and at Oberhausen-Holten certain of the later plants were erected for operation at 5–15ats gauge pressure and some of the older plants were enlarged by the addition of a "medium pressure" section.

All the plants employed a synthesis catalyst based on cobalt, and although a great volume of research work was carried out by Ruhrchemie, the Kaiser Wilhelm Institute, IG Farbenindustrie AG, the Lurgi Gesellschaft für Wärmetechnik (Metallgesellschaft AG) and several of Ruhrchemie's licensees, on new processes, and particularly on the use of iron catalysts, no new plants were erected during the war years and no extensions or significant modifications of the existing plants or of their method of operation took place.

The key personnel of companies operating Fischer-Tropsch plants were strongly of the opinion that under conditions of normal peace-time economy the process should be utilised for the production of aliphatic chemicals and special products such as waxes and high-grade lubricants, rather than fuels.

Although much of the work on new processes and catalysts was thoroughly investigated on the pilot-plant scale and in certain cases was on the point of being translated to the full scale when the end of the war came, it has been considered desirable in this report to differentiate clearly between processes which had actually been in operation on the full scale and those which had not. The latter therefore are described separately in Section D4. Sections D1–3 deal only with processes carried out on an industrial scale.

2. INDUSTRIAL OPERATION OF THE PROCESS

Although the procedure used at each of the plants varied in detail, the main features were common to all plants, and it is possible to give a general account of the method of operation.

The process can be sub-divided into the following steps:—the preparation of the gas mixture, purification of the gas mixture, synthesis in the presence of cobalt catalyst in two or more stages, condensation and collection of the primary products and their separation and working up into marketable products. These stages are described more fully below. A diagrammatic flowsheet for the synthesis at normal and medium pressures using coke as raw material is given in Fig. 51.

i. PRODUCTION OF SYNTHESIS GAS

In the presence of a cobalt catalyst, the synthesis reaction can be expressed as follows:—

$$n(2H_2 + CO) \longrightarrow (CH_2)_n + nH_2O$$
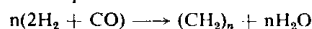
and the synthesis gas used always contained hydrogen and carbon monoxide in approximately the proportions 2 : 1. Although a large number of processes for the production of such a gas mixture direct from coal have been described in the technical literature, only two of the Fischer-Tropsch plants derived their synthesis gas by such methods. The remainder employed coke as the raw material and increased the hydrogen content of the water gas produced either by partial conversion of the CO with steam to CO_2 and hydrogen by the well-known catalytic process, or by cracking coke-oven gas either in the water gas generator or in separate cracking stoves.

Coke was the favoured raw material, partly because of its availability, but also because it could be gasified in simple and relatively trouble-free equipment and the resulting water gas was clean and easy to purify from sulphur compounds. Synthesis gas prepared by the gasification of coal or lignite tends to contain resin-forming products of coal distillation, which interfere with the subsequent catalytic removal of organic sulphur compounds, and also cyclic sulphur compounds such as thiophene which are difficult to remove.

In the production of synthesis gas from coke alone, water gas was produced in standard Humphreys and Glasgow type generators with a dry coke consumption of 0.6 to 0.7kg/m³. The H_2 : CO ratio of the water-gas averaged 1.25 : 1 and the inert content, 10–12%. Approximately one-third of the water gas (after purification as described later) was converted with steam at 500°C over an iron catalyst promoted with calcium, magnesium and chromium oxides, to give a gas containing 61%H_2 and 5%CO. When blended with the unconverted water gas, synthesis gas containing hydrogen and carbon monoxide in the proportions of 2 : 1 and 20–22% of inert constituents was obtained. From one volume of water gas approximately 1.1 volumes of synthesis gas were obtained.

Where coke and coke oven gas were used as raw materials, the coke oven gas was in one case introduced together with steam in the back-run of the cycle in standard water gas generators. In the production of 1m³ of synthesis gas (H_2 : CO = 2 : 1) containing 15% inert constituents 0.49kg coke (8% moisture) and 0.32m³ of coke oven gas were consumed. Where the coke oven gas was thermally cracked with steam in a separate cracking plant, two volumes of water gas were mixed with one volume of cracked gas to give synthesis gas of similar composition.

The processes used for the direct production of synthesis gas from coal and lignite, and further details of the above processes, are given in Section B of this report.

ii. PURIFICATION OF SYNTHESIS GAS

The synthesis gas produced from German coke contained from 2–5gm H_2S/m^3 and from 10–20gm organic sulphur compounds/100m³, and to prevent rapid poisoning of the synthesis catalyst it was necessary to remove these impurities as completely as possible.

The purification took place in two stages. Hydrogen sulphide was first reduced to about 1gm/100m³ by the conventional method of passing the gas through iron oxide at normal temperatures.

The removal of organic sulphur was then effected by passing the gas through specially designed towers containing granules prepared by mixing 70 parts of Luxmasse (hydrated iron oxide obtained as by-product in the manufacture of aluminium) with 30 parts of soda ash. The plant consisted of a number of parallel streams

FIGURE 51

COKE

WATER GAS
GENERATION.

HOLDER.

H2 S.
REMOVAL

BLOWERS

ORGANIC
SULPHUR
REMOVAL.

NORMAL PRESSURE
SYNTHESIS.

MEDIUM PRESSURE (9-11ATM)
SYNTHESIS.

STEAM → CATALYTIC CONVERSION.

COMPRESSION

SYNTHESIS I

SYNTHESIS I

COMPRESSION.

CONDENSER

CONDENSER

PREHEATER

CO2 REMOVAL
(WATER-WASH).

PREHEATER

SYNTHESIS II

SYNTHESIS II

CONDENSER

CONDENSER

PREHEATER

SYNTHESIS III

CONDENSER

CONDENSER

EXPANSION

ACTIVE
CARBON.

ACTIVE
CARBON.

FUEL GAS   PRIMARY
PRODUCTS.

FUEL GAS   PRIMARY
PRODUCTS.

FLOW-SCHEME FOR NORMAL AND MEDIUM-PRESSURE SYNTHESIS
(As operated by Ruhrchemie AG)

each of two towers in series, the gas throughput through each pair of towers being about 20,000m³/hr, and the space velocity about 200/hr. The gas was preheated in heaters fired with residual gas from the synthesis process so that the temperature in the purifying mass was maintained at 180–250°C, the temperature being increased as the contact mass approached exhaustion. Each tower contained about 60te contact material, and approximately every six weeks one tower of the pair was recharged with fresh material and was then placed behind the unchanged tower in the stream. Thus each charge of material remained on stream for about 12 weeks and absorbed in that time about 9% of its weight of sulphur. For efficient operation it was essential to ensure that the gas entering this plant contained about 0·2% of oxygen, and under these conditions the sulphur was retained in the contact mass as sodium sulphate. The heat requirement of the process was about 110k.cal/m³ gas purified.

The above process reduced the organic sulphur content of the gas to about 0·5gm/100m³. In recent years it had been customary to pass the gas through a final purification tower containing the same contact material but without any additional supply of heat, the sensible heat in the gas leaving the main purification system being sufficient to maintain a temperature of 150–180°C in this stage. The material in this final purifier lasted for two years without changing, and reduced the sulphur content of the gas to between 0·05 and 0·2gm/100m³.

The purified gas then passed to the synthesis reaction vessels with or without compression according to whether the normal or medium pressure process was being employed.

iii. SYNTHESIS PROCESS

a. The Catalyst

The catalyst developed by Fischer at the Kaiser Wilhelm Institute contained cobalt, thorium oxide and kieselguhr in the weight proportions: 100 : 18 : 100. When Ruhrchemie took over the development of the process they found that the cobalt and thoria contents could with advantage be reduced and when the full-scale plants were first put into operation a catalyst of the composition Co 100 : ThO$_2$ 15 : kieselguhr 200 was used. Further research led to the discovery that magnesia was a particularly valuable promoter for cobalt catalysts and the best all-round catalyst was found to be one of composition Co 100 : ThO$_2$ 5 : MgO 8 : kieselguhr 200. This catalyst was in use in all the German plants from 1938 onwards for both normal and medium pressure operation.

The catalyst was prepared by pouring a boiling solution of cobalt, thorium and magnesium nitrates into a boiling solution of sodium carbonate with violent agitation, adding the dry kieselguhr powder and filtering the resultant slurry. The filter cake was washed to remove the bulk of occluded sodium salts, dried and granulated, the 1–3mm size being retained for use.

Before use in the synthesis, the catalyst must be reduced in hydrogen. This step in the process was apparently the most critical. It was necessary to obtain a 60% reduction of the cobalt to the metallic state in the shortest possible time at the lowest possible temperature. This was achieved in practice by using a shallow bed of catalyst (800 litres of granules in a bed 30–35cm deep) and circulating preheated ammonia synthesis gas (H$_2$: N$_2$ = 3 : 1) carefully freed from moisture and oxides of carbon through the catalyst at a space velocity of 6,000–8,000/hr for a period of 40–60min at a temperature of 400–430°C. After cooling in nitrogen the

reduced catalyst was stored and transported in an atmosphere of CO$_2$ in vessels known as "Kübels" which held about 3te of catalyst.

When the catalyst had seriously diminished in activity through use in the synthesis process it was treated with nitric acid and the cobalt and thorium recovered for use in the preparation of fresh catalyst.

Owing to the large quantities of catalyst required in a full-scale Fischer-Tropsch plant these processes of catalyst manufacture and recovery formed an important part of the whole operation, and special factories were built for the purpose. There were three such factories

FIGURE 52

(A) REACTION VESSEL FOR NORMAL PRESSURE SYNTHESIS.

(B) REACTION VESSEL FOR MEDIUM PRESSURE SYNTHESIS.
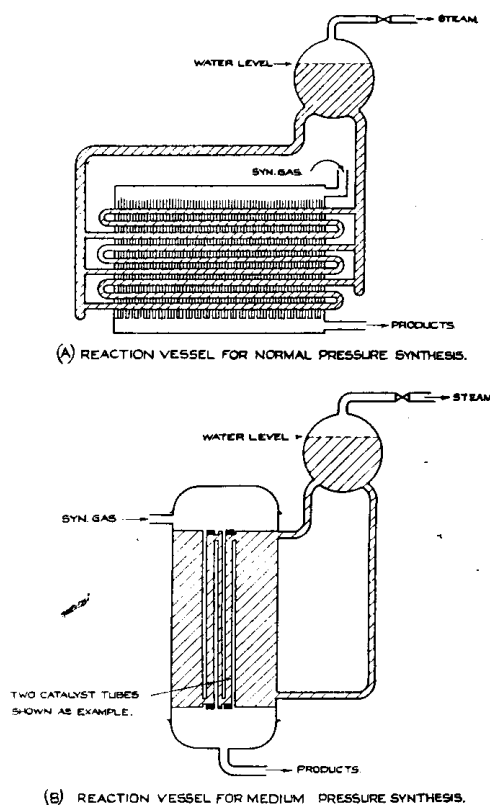
DESIGN OF REACTION VESSELS
(Diagrammatic)

in Germany, one on the Ruhrchemie site at Holten, one at the works of the Wintershall AG at Lützkendorf and a third at Ruhland-Schwarzheide (Brabag). The Ruhrchemie factory supplied all six Fischer-Tropsch plants in the Ruhr area and had an output of about 3,000te/yr reduced catalyst.

b. The Reaction Vessels

For synthesis at normal pressure the reaction vessel took the form of a rectangular sheet-steel box, approximately 5m long, 2·5m high and 1·5m wide, containing a bundle of horizontal tubes interlaced by vertical steel sheets. The tubes were arranged lengthwise, were 40mm in diameter, 40mm apart and were 600 in number. They were expanded into 555 vertical steel sheets, 1·6mm thick and 7·4mm apart. The empty vessels weighed approximately 50te. The catalyst granules were disposed in the spaces between the tubes and

sheets and occupied a volume of about 12m³. One charge of catalyst weighed about 3te and contained 850–950kg cobalt. The tubes were connected to a steam drum, which in some cases was common to two or three catalyst vessels, and the temperature in the vessels was controlled by the circulation of water through the tubes, the pressure in the water system determining the temperature. The heat of the synthesis reaction (about 600k.cal/m³ of synthesis gas treated) was thus to a large extent recovered as steam which was withdrawn from the steam drums for use on the works. The arrangement is shown diagrammatically in Fig. 52.

This rather complicated design of reaction vessel was necessary in order to prevent any local rise of temperature in the catalyst bed. If this occurs, the production of liquid hydrocarbons almost ceases and methane, carbon dioxide and carbon become the main products of the reaction. The total cooling surface of the above described vessel was 4,000m², 10% of this being direct water-cooled tube surface.

For the synthesis at 5–15ats a vessel of quite different design was used. It consisted of a vertical cylindrical steel shell 6·9m high and 2·7m internal diameter, wall thickness 31mm containing 2,100 tubes 4·5m long, 44/48mm diameter, each fitted with a concentric inner tube 22/24mm communicating with the main space in the shell through T-connections at each end of the outer tube. These latter were welded to tube plates at each end of the shell and the annular space between inner and outer tube communicated with the space above the upper and below the lower tube plates. The catalyst filled this annular space and the cooling water circulated from the steam drum through the main space in the shell and through the inner tubes. The arrangement is shown diagrammatically in Fig. 52.

The weight of the empty vessel was approximately 50te and its catalyst capacity 10m³. A block of four converters was connected to a common steam drum. The total cooling surface of each converter amounted to 2,100m², all of it directly water-cooled.

c. Operation of the Process at Atmospheric Pressure

It was general practice to operate in two stages with approximately two-thirds of the reaction vessels in Stage I and the remainder in Stage II. Between 5% and 10% of the total number of vessels were off stream at any given time for catalyst reactivation or catalyst replacement. On the average, one reaction vessel was on stream for every 650te annual production of primary liquid products. The throughput of synthesis gas in Stage I averaged 1,000m³/hr per reaction vessel and for the two stages together, 660m³/hr per vessel. The overall space velocity was therefore about 60/hr. Newly recharged reaction vessels were placed on stream in Stage II for a period which varied from one to three months and were then transferred to Stage I. The total life of a charge of catalyst varied from four to eight months, depending on the conditions and operating methods used at each plant. The reaction temperature used for a fresh catalyst was in the range 180–185°C and as the catalyst aged, the temperature was raised to a maximum of about 200°C. The average temperature in Stage I was about 195°C and in Stage II about 190°C. The activity of the catalyst in Stage I reaction vessels was maintained by periodic treatment with synthetic middle oil or by passing hydrogen for a few hours at about 195°C or by a combination of both treatments. The treatment was designed to remove (or reduce in amount) the high molecular-weight hydrocarbons retained by the catalyst. The exact procedure

employed varied from works to works. No reactivation treatments were given in Stage II.

The contraction in gas volume (an approximate measure of the extent of conversion) in the first stage was usually 50% and the overall contraction for both stages 70–75%.

d. Operation of the Process at Medium Pressure

During the last two years the medium pressure process has been operated in three stages, in place of the two formerly employed, and with approximately half the reaction vessels in Stage I, one-third in Stage II and one-sixth in Stage III. The working pressure was 9 to 11ats (gauge) and the temperature was similar to that used at normal pressure, viz. 180–200°C. Best results were obtained by using a gradation of H_2 : CO ratios in the gas entering the three stages, i.e. in Stage I, H_2 : CO = 1·4–1·6, in Stage II, 1·6 and in Stage III, 1·8. This result was achieved by compressing the water gas and converted gas (hydrogen-rich gas) separately and adding the requisite amount of converted gas before each synthesis stage. The input gas rate to Stage I and the overall gas throughput were similar to those used in normal pressure synthesis, i.e. about 1,000m³/hr and 650–700m³/hr per reaction vessel respectively. A fresh charge of catalyst was normally used initially in Stage III or II and was moved forward as it aged, depending on the requirements of the earlier stages. The total life of one charge of catalyst was between six and nine months. No reactivation treatments with solvent or hydrogen were employed in the medium pressure synthesis. The gas contractions in the three stages were approximately 50%, 35–40% and 30% respectively, giving an overall contraction of 75–78%.

e. Condensation and Collection of Products

In the normal pressure process the hot gases leaving the bottom of the reaction vessels were cooled by direct contact with water sprays in packed towers lined with acid-resisting brickwork, where the fraction of oil boiling above about 145°C was condensed. The cooled gases and vapours were then passed through an active charcoal absorption plant of normal type where the low-boiling liquid hydrocarbons and the bulk of the C_3 and C_4 hydrocarbons were removed and were recovered by steaming in the usual manner. To ensure adequate recovery of C_3 and C_4 hydrocarbons the charcoal plant was operated to an absorption of 3%wt of hydrocarbons calculated as carbon. In some plants both condensation and charcoal absorption were carried out between the stages, but in others the condensation of the heavier oil only was practised, the lighter oil vapours passing through the second stage of synthesis, and only the one charcoal absorption plant at the outlet of the last stage condensers being used.

In the medium pressure process about 35% of the reaction product leaves the reaction vessel in the liquid state and after separation from this fraction the gases were passed through a simple indirect tubular-type condenser constructed of acid-resisting alloy steel. The gases were then, in most cases, expanded to normal pressure and passed through active carbon absorbers. Up to a pressure of 10ats this procedure was considered the more economic, but at higher pressures removal of the light oils and condensable gases by oil washing before dropping the pressure to atmospheric was thought to be preferable. Condensers only were employed between the stages.

The refining of the products was similar in both cases. The liquid products recovered by condensation and by

TABLE L

PRODUCTS FROM THE FISCHER SYNTHESIS

	Normal pressure process		Medium pressure process	
	% wt of total	Olefin content % vol	% wt of total	Olefin content % vol
Condensable gases (C₃ and C₄)	14	45	10	40
Light oil 25–165°C	47	37	26	24
Middle oil 165–230°C	17	18	} 37	9
Heavy oil 230–320°C	11	8		
Soft wax 320–460°C	8	—	17	—
Hard wax > 460°C	3*	—	10	—

* Extracted from the catalyst.

steaming the active carbon were stabilised, cut into broad fractions by distillation and the liquid fractions washed with alkali solution to remove fatty acids.

f. Yield and Composition of Products

The yield of useful products, *i.e.* C₃ and higher hydrocarbons obtained in two-stage operation at normal pressure varied from 130 to 165gm/m³ inert-free synthesis gas (*i.e.* H₂ + CO) compared with a theoretical production of 208gm/m³. Production varied from 500 to 720te/yr per reaction vessel and from 200 to 530te/te of cobalt introduced. The corresponding figures for synthesis in three stages at 9–11ats were 145–160gm/m³ H₂ + CO, 600–750te/yr per reaction vessel and 350–630te/te Co. The average composition of the primary products of the two processes in the fractions in which they were normally separated in recent years is given in Table L.

The products consist mainly of straight-chain hydrocarbons, although there were statements that some isobutylene was present in the C₄ fraction and evidence that the wax contained isohydrocarbons. Very little ethane or ethylene was produced in the synthesis. The production of methane + C₂ was about 14% of the total hydrocarbon production for atmospheric pressure synthesis and about 10% for the medium pressure process. These hydrocarbons, together with a small amount of C₃ and C₄ hydrocarbons, remained in the residual gas which varied in composition and calorific value, mainly due to variation in the amount of inerts and methane in the original synthesis gas.

iv. PROPERTIES AND USES OF PRIMARY PRODUCTS

a. Condensable Gases

The C₃ and C₄ hydrocarbons were liquefied by compression and sold in cylinders and tank cars, except in one case (Rheinpreussen), where about one-third of the production was converted into alcohols.

b. Light Oil

The stabilised petrol was despatched without further treatment to various blending stations where it was used as base stock in the preparation of motor fuel.

Typical inspection data for this fraction were as follows: —

Sp.gr		0·683
Vapour pressure (ats)		0·59
% off at 75°C		40
FBP, °C		165
Octane no. (Motor)		53

These figures relate to the fraction from atmospheric pressure synthesis. The corresponding fraction from the medium pressure process had similar properties apart from the octane number, which was only 45.

At the blending station it was usually mixed with not less than 20% of benzole and from 0·02 to 0·04% TEL to produce an Army motor fuel of octane number 72 to 78.

c. Middle Oil

The fraction 165–230°C was also sent to blending stations for use as a high-grade diesel oil component. The properties of this fraction were as follows:—

	Synthetic diesel oil	Mixed diesel oil
Sp.gr	0·748	0·848–0·880
Solidifying point °C	−40	−35 to −26
Flash point °C	45	63
Cetane no.	78	55–48
Boiling range °C	164–238	170–280/320

The synthetic oil was used at the blending stations primarily for the production of aviation diesel oil for the Luftwaffe by blending with an equal weight of petroleum oil.

At the Rheinpreussen works a mixed diesel oil of the properties shown above was produced by blending approximately equal volumes of the synthetic middle oil and coal-tar middle oil. The mixture was treated successively with weak mineral acid and weak alkali (to accelerate the separation of asphaltic material and to remove phenols), then centrifuged, treated with bleaching earth and filtered.

d. Heavy Oil

Originally, the entire fraction 170–320°C had been used as diesel fuel, but due to the acute shortage of soap during the war the heavy end (230–320°C) of this fraction had been sent to IG for conversion into "Mersol" detergents (see later).

e. Waxes

The bulk of soft wax, or "Gatsch," as it was called, was despatched to the Deutsche Fettsäure Werke, Witten, for conversion to fatty acids, and the hard wax sold mainly to wax blenders and users.

The Ruhrchemie works at Holten had installed a wax-refining plant to produce various finished grades of wax. The residue above 320°C from the distillation of the primary product of the medium pressure synthesis was separated by vacuum fractionation into two distillates and a residue distilling above 460°C (760mm). The first fraction was "sweated" to give "soft wax" (mp40°C), the second fraction was sweated to mp50–52°C to yield "slab wax." The residue (crude "hard wax") mp90°C, was refined with bleaching earth and sold as "refined hard wax." By blending 30 parts of this wax with 70 parts soft wax a product sold as "refined plastic wax" was obtained.

By similar treatment of the residue above 320°C obtained from the distillation of products from the normal pressure process and the wax extracted from the

TABLE LI

RUHRCHEMIE-FISCHER-TROPSCH WAXES—PROPERTIES, QUANTITY SOLD AND PRICE
OBTAINED DURING THE YEAR JULY, 1942, TO JUNE, 1943

Grade							Soft wax	Slab wax	Catalyst wax	Refined plastic wax	Refined hard wax
Properties:—											
Setting point (rotating thermometer)			°C	42·5	50–52	87–91	75	90
Melting point..					°C	44·0	53	—	ca85	110
Flow-point					°C	40·2	48–49	—	77	98
Drop-point					°C	41·8	49–50	—	79	99
Iodine no.						—	2·5	3·5	2·0	2·0
Acid no.						0·14	0·03	—	0·05	0·1
Saponification no.						0·35	0·6	1·0	0·9	0·8
Penetrometer no.						—	35·0	ca30	17·0	4·0
Mean mol wt						—	380	—	500	600
Mean carbon no.						—	27	—	36	43
Sales:—											
Quantity					te	356·48	718·68	1,382·34	281·95	5,731·13
Price					pfg/kg	50·1	56·4	66·9	119·7	94·4

TABLE LII

ANNUAL PRODUCTION OF PRIMARY PRODUCTS (INCLUDING $C_3 + C_4$ GASES)

(Tonnes)

Year	Ruhr-chemie	Rhein-preussen	Gewerk-schaft Viktor	Krupp Treib-stoffwerk	Essener Stein-kohle	Hoesch-Benzin	Brabag	Winter-shall	Schaff-gotsch	Total all plants
1938	27,443	28,542	27,140	*	*	*	103,503	*	*	186,628
1939	49,371	54,684	31,192	31,795	35,715	15,635	116,990	*	*	335,382
1940	58,728	70,163	35,903	40,094	61,510	37,297	151,380	*	*	455,075
1941	57,145	73,271	37,740	48,355	74,465	46,719	149,120	*	18,609	505,424
1942	62,684	71,560	37,701	49,950	83,465	48,150	162,270	*	26,377	542,117
1943	46,273	70,250	39,834	54,020	83,651	39,781	179,665	22,045	33,658	569,179
1944†	62,200	69,700	40,380	39,802	86,580	51,000	158,500	29,320	39,200	576,682

* Figures are not available in these cases but are believed to be small, as the plants in question were only in experimental operation at the time.
† Yearly production based on production over first 6 months.

catalyst by solvent, further quantities of soft wax and a moderately hard wax sold as "catalyst wax" were obtained.

The properties of these waxes, the amounts sold during the year 1942–1943 and the price obtained for them by Ruhrchemie are shown in Table 1. The hard wax and slab wax were used in the manufacture of polishes, candles and explosives. The so-called plastic wax was used for impregnation of paper and cardboard.

f. Fatty Acids and Alcohols

The water formed in the synthesis contains small amounts of the lower fatty acids. In some works these were recovered by neutralisation of the water used in the direct coolers. Rather more acids were obtained in the medium pressure process (about 0·5–1% of the total products) and about half the total amount was in the range C_{11}–C_{18}. In view of the soap shortage it became general practice to recover these higher acids, and at Holten about 36te/yr were recovered and converted into soap.

Small amounts of ethyl, propyl and butyl alcohols were also produced in the medium pressure synthesis, and at the Hoesch-Benzin works about 1te/day was recovered from the condensate water.

g. Residual Gas

The tail gas from the synthesis process was used as

fuel on the works, e.g. for the organic sulphur purifiers, stills, power station, coke ovens, etc.

v. PRODUCTION DATA AND PROCESS CHARACTERISTICS OF THE VARIOUS PLANTS

The locations and names of the operating companies of the nine Fischer-Tropsch plants were as follows:—

(1) Oberhausen-Holten (Sterkrade-Holten), Ruhr, Ruhrchemie AG.

(2) Moers-Meerbeck (Homberg), Niederrhein, Steinkohlen-Bergwerk Rheinpreussen.

(3) Castrop-Rauxel, Ruhr, "Gewerkschaft Viktor," Klocknerwerke AG.

(4) Wanne-Eickel, Ruhr, Krupp Treibstoffwerk GmbH.

(5) Kamen-Dortmund (Bergkamen), Ruhr, Chemische Werke Essener Steinkohle AG.

(6) Dortmund, Ruhr, Hoesch-Benzin GmbH.

(7) Ruhland-Schwarzheide, Dresden area, Braunkohle-Benzin AG (Brabag).

(8) Lützkendorf-Mücheln, Leipzig area, Wintershall AG.

(9) Deschowitz-Beuthen, Odertal (Upper Silesia), Schaffgotsch Benzin GmbH.

TABLE LIII

OPERATING DATA FOR THE MONTH OF JANUARY, 1944

	1		2	3	4	5	6	7	8	9
Operating company	Ruhrchemie		Rhein-preussen	Gewerk-schaft Viktor	Krupp Treib-stoffwerk*	Essener Stein-kohle	Hoesch-Benzin	Brabag	Winter-shall	Schaff-gotsch
Type of Process	Normal pressure	Medium pressure	Normal pressure	Normal pressure	Stage I, normal pressure; Stage II, medium pressure	Normal pressure	Medium pressure	Normal pressure	Normal pressure	Medium pressure
Synthesis gas used .. m³	13,055,000	32,600,000	48,029,000	23,204,000	37,566,000	54,267,000	33,530,000	118,488,000	22,579,000	25,930,000
Inert content of synthesis gas %	20·0	13·4	19·0	14·1	18·8	16·2	14·0	20·0	24·7	17·2
Number of stages ..	2	3	2	2	2	2	3	2	2	3
Number of reaction vessels on stream	35·9	61·8	89·6	50·4	69·3	114·7	65·0	230·7	66·1	58·9
Gas throughput (all stages) .. m³/hr/vessel	492	714	721	609	726	636	692	690	464	586
Overall gas contraction %	64·9	75·7	68·2	75·8	67·6	73·6	77·6	70·5	65·8	71·0
Yield gm/m³ H₂ + CO (excluding C₃ and C₄)	120·4	135·1	129·2	138·2	119·0	150·9	145·0	141·5	100·6	139·9
Yield gm/m³ H₂ + CO (including C₃ and C₄)	132·6	144·5	146·3	155·8	138·2	165·0	161·1	163·9	127·1	150·2
Total production (including C₃ and C₄) te	1,382·1	4,068·0	5,695·0	3,109·6	4,157·0	7,504·0	4,620·0	15,560·5	2,155	3,236
Production/reaction vessel/month .. te	38·5	65·8	63·5	61·7	59·4	65·4	71·0	67·4	32·6	55·0
Production/catalyst charge .. .. te	162	401	285	328	310	469	495	241	66	—
Catalyst life months	4·2	6·1	4·5	5·3	5·2	7·2	7·0	3·6	2·0	—

* Data for December, 1943 (data for January, 1944, not available).

The annual production of total primary products in these plants for 1938–1944 is shown in Table LII and the more important operating data for January, 1944, in Table LIII. A brief account of the main features of the plants is given below.

a. Ruhrchemie AG

Synthesis gas was produced from oven coke via water gas and catalytic conversion. Synthesis took place in two independent systems, one operating in two stages at normal pressure and the other in three stages at medium pressure (9–11ats). The normal H_2 : CO ratio of 2 : 1 was used in the normal pressure system and ratios of 1·4 : 1, 1·6 : 1 and 1·8 : 1 respectively, for the three stages in the medium pressure system. The rather poor performance of this plant compared with certain of the others was attributed by the Company to the constant experimentation which took place at this "parent" plant.

b. Rheinpreussen

This concern operated their own coke ovens and utilised their spare coke oven gas in the production of synthesis gas. Normally, water gas was produced from oven coke, 18% of the total was catalytically converted and the product blended with the remainder. This blended gas was then mixed with about one-third of its volume of "cracked gas" produced by cracking coke oven gas with steam at 1,200°C by the Koppers process in Cowpers. The synthesis plant was a normal pressure two-stage system. The method of operation differed from that at other plants, in that a rather higher throughput per reaction vessel was employed, a larger proportion of the vessels were in Stage I, and the catalyst was deliberately run to a shorter life (4–4½ months).

c. Gewerkschaft Viktor

This Company also had its own coking plant and prepared synthesis gas by blending two volumes of coke water gas with one volume of cracked coke oven gas. The cracking in the presence of steam was carried out at 1,350–1,400°C, in plant designed by the Company, but which appeared to be very similar to the Koppers plant.

The synthesis system comprised two stages at atmospheric pressure. The catalyst life was normally 5½ months.

d. Krupp Treibstoffwerk

Water gas was produced from coke (80% oven coke, 20% low-temperature coke produced by the Krupp-Lurgi process) and one-third of the total catalytically converted to give synthesis gas (H_2 : CO = 2 : 1). The synthesis plant used a mixed normal pressure–medium pressure system. The synthesis gas passed first through one stage at atmospheric pressure and the residual gas after passing through both condensers and active carbon absorbers was compressed to 9–10ats and passed through one stage of medium pressure. Of the 24 medium pressure reaction vessels, 16 were of a novel type. The double-tube assembly was replaced by single tubes 72mm internal diameter fitted with internal fins of sheet metal. This arrangement increased the catalyst capacity of the vessel by 5%, but the difficulties experienced in discharging the catalyst suggested that carbon deposition occurred in this type of vessel.

e. Essener Steinkohle AG

In this plant coke oven gas was cracked in the back-run of the cycle in normal water gas generators using oven coke to give synthesis gas (H_2 : CO = 2 : 1) in one step. As there was a tendency for thiophene and resin-forming hydrocarbons from the coke oven gas to pass through into the synthesis gas, active carbon absorbers were inserted in the stream between the removal of H_2S and the removal of organic sulphur.

Synthesis took place in two stages at normal pressure with active carbon absorbers in addition to the normal condensers between the stages.

This plant appears to have been exceedingly well managed and consistently achieved the highest conversion

TABLE LIV

SYNTHESIS AT NORMAL PRESSURE (CHEMISCHE WERKE ESSENER STEINKOHLE AG)
CONSUMPTION OF MATERIALS AND ENERGY DURING THE YEAR JULY, 1942, TO JUNE, 1943, IN THE
PRODUCTION OF 82,203·77 TE OF FINISHED PRIMARY PRODUCTS

(Equivalent to 82,470·43 te crude total primary product ≡ 159·7gm/m³ inert-free synthesis gas)

Item		Total consumption	Required from outside sources
Coke (7·8% moisture, 6,571k.cal/kg)	te	306,832	306,832
Coke oven gas (4,985k.cal/m³)	m³	214,761,900	214,761,900
Electricity	kwh	49,301,415	16,402,665
Steam at 3·5ats	te	795,893	—
„ 10ats	te	284,225	2,796
„ 23ats	te	413,841	—
Canal water	m³	2,201,671	2,201,671
Mains „	m³	2,208,493	2,208,493
Feed „	m³	1,142,378	1,142,378
Fischer-Tropsch catalyst	te	519·05	519·05
Luxmasse (for H₂S removal)	te	3,500·0	3,500·0
Organic sulphur mass	te	1,440·0	1,440·0
"Desorex" active carbon (for gas purification) ..	te	15·0	15·0
Active carbon (for spirit recovery)	te	1,683·44	1,683·44
Alkazid solution (for CO₂ removal)	m³	6,556	6,556
Surplus recovered energy—			
Residual gas from the synthesis—			
Total produced (at 3,912k.cal/m³)	m³	172,639,300	
Utilised on the works	m³	13,747,400	
Surplus returned to adjacent colliery for heating			
coke ovens	m³	158,891,900	—
Steam—			
Surplus returned to colliery at 3·5ats	te	36,569	
„ „ „ „ „ 10ats	te	64,022	

per m³ and the highest space-time output of all the plants operating at normal pressure. This may have been due to several causes: the high degree of purification of the gas and its low inert content; a more equal distribution of catalyst between the two stages; the use of a rigid schedule for the treatment of a newly recharged vessel with respect to temperature; duration of the catalyst in each stage; and the method and frequency of reactivation of the catalyst with solvent and hydrogen. Ruhrchemie and other plant operators, however, attributed the success of this plant to constant gas composition and throughput and to freedom from interruptions and breakdowns rather than to any intrinsic merit in their method of operation.

f. Hoesch-Benzin GmbH

Synthesis gas was produced from coke via water gas and catalytic conversion. This plant operated entirely at medium pressure (10ats). Originally two stages only were employed but in recent years the system was increased to three stages, using synthesis gas with H₂ : CO ratio 1·6 : 1 in all stages, converted water gas being added to the end gas from Stages I and II to maintain this ratio.

Contrary to the practice at other plants newly-charged reaction vessels were put on stream in any stage.

g. Brabag

This plant was the largest Fischer-Tropsch plant ever erected. It comprised 262 reaction vessels and its maximum annual output was 162,000te of primary products.

The plant was in the zone occupied by the Russian Armies and has not been visited by British or American investigators, but Ruhrchemie documents have provided some information concerning the details of operation.

Synthesis gas was produced from brown coal briquettes partly by gasification in Didier-Bubiag externally-heated retorts (one-fifth of total) and partly by the Koppers

process (four-fifths of total). Due to the low sulphur content of the brown coal, the purification of the gas gave no difficulty despite the presence of some resin-forming compounds. The synthesis system consisted of two stages at atmospheric pressure. Newly-charged reaction vessels were started in either stage but were not switched from one to the other; they were run until a fixed quantity of synthesis gas had been passed —irrespective of catalyst activity. The cycle for reactivation with solvent and hydrogen was based on that used by Essener Steinkohle and the yield and conversion data available indicate that the plant rivalled the latter's in efficiency.

h. Wintershall AG

Except for the last two years of operation, this plant was a complete failure. This was almost entirely due to the fact that it relied for its supply of synthesis gas on the first full-scale Schmalfeldt generator to be erected. This generator produced synthesis gas of H₂ : CO ratio 2 : 1 by the direct gasification of powdered brown coal, but was really only in the experimental stage. The sulphur content of the gas was exceedingly high and until active carbon absorbers were inserted in the purification stream, the life of the synthesis catalyst was only 1½–2 months. During the period of compara-tively satisfactory operation, the synthesis gas contained 25% inert constituents and the yield of total primary products was 130gm/m³ CO + H₂. The maximum output obtained was 30,000te/yr, *i.e.* only 40% of the planned production.

The synthesis plant comprised two stages operating at atmospheric pressure. Although 132 reaction vessels were installed the maximum number maintained on stream during any one month was 77.

i. Schaffgotsch-Benzin

This plant was also outside the zone open to British and American visitors and the available information has been obtained from Ruhrchemie documents.

TABLE LV

HEAT BALANCE AND THERMAL EFFICIENCY DATA FOR THE SYNTHESIS

(For the month of May, 1944)

Operating company	Essener Steinkohle AG		Ruhrchemie AG			
Type of process	Normal pressure		Normal pressure		Medium pressure	
Monthly production of total primary products .. kg	6,842,050		1,511,880		3,865,430	
Yield on inert-free synthesis gas gm/m³	160·3		129·6		140·6	
	k.cal/kg total primary products	% of ingoing heat	k.cal/kg total primary products	% of ingoing heat	k.cal/kg total primary products	% of ingoing heat
Ingoing heat as :						
Coke ..	24,078	63·2	43,573	92·6	40,164	80·3
Coke-oven gas	11,578	30·4	—	—	—	—
Electricity	1,037	2·7	1,306	2·8	7,616	15·2
Steam ..	1,370	3·7	2,145	4·6	2,236	4·5
TOTAL ..	38,063	100·0	47,024	100·0	50,016	100·0
Recovered heat in :						
Primary products	11,260	29·6	11,260	24·1	11,260	22·5
Residual gas ..	7,627	20·2	6,196	13·2	3,775	7·6
Steam ..	2,210	5·8	2,804	6·0	2,804	5·6
Loss ..	16,966	44·4	26,674	56·7	32,177	64·3
TOTAL ..	38,063	100·0	47,024	100·0	50,016	100·0
Heat recovered as primary products, % of heat put in as coke and coke-oven gas	31·6		26·0		28·0	
Total heat recovered in useful form, % of total ingoing heat	55·6		43·3		35·7	
Net heat consumed in the production of 1kg primary products .. k.cal	28,226		37,934		43,437	
Calculated as kg ash- and moisture-free coke of CV = 8,000k.cal/kg ..	3·55		4·75		5·43	
Measured consumption of ash- and moisture-free coke per kg of primary products	—		5·64		4·94	
Calculated as coke of CV = 7,000k.cal	4·05		5·42		6·20	
Calculated as coal of CV = 7,000k.cal assuming 90% thermal efficiency of conversion of coal to coke ..	4·5		6·02		6·89	

Synthesis gas was made from hard coke and coke oven gas in Pintsch generators. The latter were considered to be less satisfactory than the type used at other plants. Up to the middle of 1943, the synthesis was operated in two stages at 10ats but was then converted to three-stage operation similar to that employed by Ruhrchemie and Hoesch-Benzin.

Of the 68 reaction vessels, 50 were of a different type from the normal. They contained single catalyst tubes 22mm and in some cases, 33mm internal diameter in place of the double-tube "annulus" type. This arrangement increased the catalyst capacity by 10% but although the Company claimed that the wide-tube vessels behaved satisfactorily, particularly in Stages II and III of the three-stage process, the catalyst in nearly all cases had to be removed by drilling, which suggests excessive carbon deposition.

vi. MATERIAL AND ENERGY REQUIREMENTS OF SYNTHESIS

The amounts of coke, coke oven gas, electricity, steam, water, catalyst and other materials consumed in a year's operation of the Essener Steinkohle plant are recorded in Table LIV. The figures cover the entire process of production of the final products, motor spirit base, diesel oil, wax, etc. The energy recovered as residual gas and steam is shown at the bottom of the table.

The energy balance for the process based on one month's operation of the above plant and also of the normal and medium pressure sections of the Ruhrchemie plant is given in Table LV.

The data given show clearly the relatively high efficiency of the Essener Steinkohle plant. This appears to be mainly due to the higher degree of conversion of synthesis gas to primary products, but is apparently also due to some extent to a higher efficiency in the manufacture of synthesis gas. The high thermal value of the residual gas is due to the fact that in the production of synthesis gas some methane in the coke oven gas escaped cracking and appeared in the synthesis gas to the extent of 4 to 5%. This methane became concentrated in the residual gas.

The low overall thermal efficiency of the medium pressure synthesis is due to the high consumption of electricity for compression. This is also the reason why the theoretical coke consumption is higher than the observed in this case.

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vii. COSTS

The information available for the capital and production costs of the plants actually in existence is rather fragmentary, and although a mass of cost information relating to projected new plants in Germany and other countries is available, this is considered to be of much less value.

a. Capital Costs

Prof. Martin, Managing Director of Ruhrchemie, gave the following figures for the capital costs of the German plants, exclusive of site preparation and services:—

Normal pressure plants: RM800/te annual production. Medium pressure plants: RM850–900/te annual production.

Dr. Bütefisch, a director of IG, who acted as one of the German Government economic advisors on oil production during the war, gave a figure of RM860/te annual production as the capital cost for Fischer-Tropsch plants, thus confirming Martin's statements.

On the other hand, the actual capital cost of the Hoesch-Benzin plant (40,000te annual output) was RM26 millions, giving a figure of RM650/te annual production and that of the Essener Steinkohle plant (80,000te annual output), RM32 millions, giving RM400/te annual production. These two plants were built later than that of Ruhrchemie and were operated more efficiently.

b. Production Costs

Catalyst manufacture and recovery.—Catalyst was normally prepared from solutions of cobalt, thorium and magnesium nitrates obtained from the regeneration of spent catalyst with the addition of make-up magnesium and fresh kieselguhr. Ruhrchemie documents give costs for the two steps of catalyst preparation and regeneration from which the total cost can be derived.

TABLE LVI

COST OF CATALYST REGENERATION (RUHRCHEMIE AG) FOR SEPTEMBER, 1943

Basis :   1kg cobalt
Output :   92·554te cobalt

						RM
Labour	..	..	..	..	..	0·28

Energy:

Electricity	2·81kwh	at RM0·02/kwh	=	0·06
Steam @ 18ats	7·96kg	at RM4·00/te	=	0·03
„ @ 2·5ats	30·98kg	at RM2·70/te	=	0·11
Fresh water	0·33m³	at RM0·07/m³	=	0·02
Heating gas	1·22m³	at RM0·027/m³	=	0·03
				0·25
				—— 0·25

Materials:

Soda ash	1·91kg	at RM82·2/te	=	0·18
Nitric acid	0·81kgN₂	at RM0·60/kgN₂	=	0·49
Distilled water	0·08m³	at RM1·24/m³	=	0·18
Sodium fluoride	0·18kg	at RM560/te	=	0·10
Sulphuric acid	0·35kg	at RM33·6/te	=	0·01
Potassium sulphate	0·11kg	at RM204·9/te	=	0·02
				0·98
				—— 0·98

Various costs:

Repairs and maintenance, transport } Laboratory services, etc. }	..	0·53

Total ..	..	..	..	..	2·04
Depreciation ..	..	..	..	..	0·51
Taxes	..	..	..	..	0·17
9% addition ("Zuschlag") ..	..	..	..	0·25
Total costs	..	..	..	..	2·97

TABLE LVII

COST OF CATALYST PREPARATION AND REDUCTION FOR SEPTEMBER, 1943 (RUHRCHEMIE AG)

Basis :   1kg cobalt
Production : 91·968te cobalt

						RM
Labour	..	..	..	..	..	0·42

Energy:

Electricity	5·09kwh	⎫	Unit	⎧ 0·10
Steam (18ats)	7·22kg	⎮	costs	⎮ 0·20
„ (2·5ats)	8·00kg	⎬	as	⎨ 0·02
Fresh water	0·22m³	⎮	before	⎮ 0·02
Heating gas	2·06m³	⎭		⎩ 0·06
				0·40
				—— 0·40

Materials:

Soda ash	2·86kg	⎫	Unit	⎧ 0·24
Nitric acid	0·11kgN₂	⎬	cost as	⎨ 0·07
Distilled water	0·27m³	⎭	before	⎩ 0·33
Nitrogen gas	0·98m³	at RM0·03/m³		0·03
CO₂	0·75kg	at RM0·07/kg		0·06
Magnesium	0·11kg	at RM0·23/kg		0·02
Ammonia synthesis gas	6·20m³	at RM0·05/m³		0·31

Credit :

Recovered synthesis gas	0·67m³	at RM0·03/m³		0·02
				1·04
				—— 1·04

Various costs:

Repairs and maintenance, various materials, laboratory services, etc.	0·90

Total ..	..	..	..	..	2·76
Depreciation ..	..	..	..	..	0·64
Taxes	..	..	..	..	0·20
9% addition ("Zuschlag") ..	..	..	..	0·32
Total costs per kg cobalt	..	..		3·92

Hence, total cost of 1kg of cobalt in the form of reduced catalyst ready for use

$$= 3·92 + 2·97 = \text{RM}6·89$$

Cost of organic sulphur removal mass.—The iron oxide-sodium carbonate contact used in all plants in Western Germany for removal of organic sulphur compounds from the synthesis gas was manufactured in the Ruhrchemie catalyst factory at Holten. The costs of manufacture in September, 1943, are given in Table LVIII.

TABLE LVIII

COST OF ORGANIC SULPHUR REMOVAL MASS RUHRCHEMIE AG, SEPTEMBER, 1943

Basis: 1te finished mass
Output: 918·61te

Raw materials:

					RM
Soda ash, 0·29te at RM82·2te	..	..	..		23·39
Luxmasse (approx. 50% H₂O), 1·34te at RM 17·85te					23·66
Wages and salaries	..	..	..	..	11·86

Energy:

Electricity, 25·638kwh at RM0·02/kwh	..	..		0·50
Steam (18ats), 3·462te at RM4·00/te	..	..		13·85

Various costs:

Laboratory services, repairs and maintenance, transport, etc.	21·71

Total	..	..	..	..	94·97
Depreciation	..	..	..	..	6·31
Taxes	..	..	..	..	1·75
10% addition ("Zuschlag")		..	..	..	10·30
Total cost per te	..	..	..	113·33

(Cost for current year (Jan.–Sept., 1943) = RM110·22).

Cost of the Synthesis Process

In the following tables, production costs for three of the Fischer-Tropsch plants are given. (Tables LIX and LX.)

TABLE LIX

SYNTHESIS PLANT COSTS, 1939–1940

RUHRCHEMIE AG

Yield = 134·4gm. primary products incl. C_3 & C_4/m^3 $H_2 +$ CO.
Production = 58,728 te/yr total primary products.

Water gas manufacture:	pfg/m³
Coke, 0·680kg/m³ (coke at RM19·5/te)	1·326
Energy	0·071
Wages and salaries	0·066
Repairs, maintenance and general works costs	0·170
	1·633

Synthesis gas manufacture and purification:	pfg/m³
Water gas : 0·915m³/m³ synthesis gas ..	1·495
Energy	0·080
Wages and salaries	0·024
Purification masses	0·056
Repairs, maintenance and general works cost	0·047
	1·702

Synthesis of primary products:	pfg/kg
Synthesis gas : 7·44m³ H_2 + CO = 9·49m³ synthesis gas at 1·702pfg/m³	16·160
Energy	0·131
Wages and salaries	0·310
Catalyst	3·789
Various materials	0·291
Repairs, maintenance, laboratories and general works costs	1·076
	21·757

Collection of products:	
Condensation, active-carbon plant, stabilisation, etc	1·809
Total cost of primary products	23·566

The data in Table LIX refer to the whole plant, *i.e.* normal pressure and medium pressure sections.

In 1941, Ruhrchemie gave the total cost of the primary products, including capital charges (depreciation and interest) and taxes as 33·0pfg/kg.

Cost of producing refined products.—The lower cost of production of the plants of Essener Steinkohle and Hoesch-Benzin compared with that of Ruhrchemie is considered to be mainly due to the much higher yields obtained and the generally higher efficiency of these two plants and to the fact that they ran as purely production plants and were not interfered with by experimental work as was the case of Ruhrchemie.

It will be noted that the slightly higher cost for Hoesch-Benzin compared with Essener Steinkohle at a point where the yield of products was the same in each case is almost entirely accounted for by the power required for compression in the medium pressure process.

All these sets of costs data show clearly that the cost of making the synthesis gas is the major item in the cost of the process. It was for this reason that the operating companies aimed at maximum conversion of the synthesis gas rather than maximum plant output.

3. INDUSTRIAL PRODUCTION OF SECONDARY PRODUCTS

Synthetic lubricating oils which were important secondary products are considered in Section G2.

i. HIGH-GRADE PETROL

In the early days nearly all the Fischer-Tropsch plants had installed thermal cracking plants (either TVP or Carburol process) for obtaining additional petrol from the high-boiling oils. The results obtained were not very promising and no cracking for petrol production had been carried out since 1939. Several plants

TABLE LX

SYNTHESIS PLANT PRODUCTION COSTS

Operating company	Essener Steinkohle AG	Hoesch-Benzin GmbH
Period	April, 1944	January, 1942
Process	Normal pressure	Medium pressure
Yield, gm total primary products/m³ H_2 + CO	163·5	164·5
Production, te/month	7,000·3	4,272·6
	pfg/kg total primary product	pfg/kg total primary product
Raw material:—		
Coke	7·70*	7·80‡
Coke oven gas	4·75†	—
Fuel, power and water .. ..·	2·46	5·35
Wages and salaries	1·08	1·20
Materials:—		
Synthesis catalyst	1·71	1·90
Other materials	0·71	1·15
Repairs and maintenance..	0·42	1·60
Various costs	1·77	1·98
TOTAL	20·60	20·98
Credit for steam and residual gas	4·37	3·48
TOTAL	16·23	17·50
Capital charges	7·48	8·31
TOTAL PRODUCTION COSTS	23·71	25·81
Cost of the sections of the process:—		
Production of synthesis gas	13·25	13·74
Purification of synthesis gas	2·45	1·41
Compression and removal of CO_2	—	2·88
Synthesis of primary products	6·55	5·42
Recovery and refining of primary products	1·46	2·36
TOTAL	23·71	25·81

* 3·75kg at RM20·68/te.   † 2·5m³ at pfg1·9/m³.   ‡ 4·38kg at RM17·79/te.

possessed polymer petrol units (either IG or UOP process) for converting the C_3 and C_4 olefines into high-grade petrol, but these also had not been operated during the war years.

No aviation petrol was prepared from Fischer-Tropsch p   ry products.

ii. SYNTHETIC SOAP AND EDIBLE FAT

Fatty acids for the manufacture of soaps and edible fat ("margarine") were produced by the Deutsche Fettsäure-Werke of Witten, Ruhr, by the oxidation of Fischer-Tropsch wax. The process was as follows.

Crude soft wax (bp approximately 325–450°C) in batches of 8–20te was oxidised in aluminium towers at a temperature of 110–120°C by blowing with air at a rate of 50m³/hr per te of wax in the presence of 0·2% of KMnO₄ as catalyst. The process was stopped when the acid number reached 70–80 (saponification no. 135–140) and the product washed with hot water to remove KMnO₄ and water-soluble acids. The product was then neutralised with sodium carbonate and saponi-fied with 38% caustic soda solution at 100°C. The undissolved layer was returned to the oxidation vessels and the crude soap solution heated to 170–180°C at 25ats for 1hr. After the separation of a further quantity of unoxidised material (returned to the oxidation stage) the soap solution was passed through a pipe still at 320°C and the resulting anhydrous liquid soap run into water, treated with sulphuric acid and the free fatty acids separated. In the pipe still, further small quanti-ties of unsaponifiable material were steam distilled off and returned to the oxidation stage. The free acids (acid no. 340, saponification no. 350) were fractionated a   mm pressure to give three distillates and a residue. The yield of these fractions (based on the wax converted) and their properties were as follows:—

the work of certain university biochemists, which was suppressed by the Nazi Government, threw considerable doubt on this. The fat always contains some esters of branched-chain fatty acids, and certain of these have been shown to be definitely toxic.

The low-boiling fatty acids found a ready market for the preparation of esters and of the corresponding alcohols. The higher acids were used as emulsifying agents in dyeing and the residual acids in the preparation of lubricating greases.

The Witten plant treated 40,000te/yr of Fischer-Tropsch wax and produced 32,000te of fatty acids. The output of finished edible fat was 150te per month. The IG had wax oxidation plants (using an almost identical process) at Oppau and Heydebreck, each of 20,000te/yr wax throughput. The raw material in these cases was partly Fischer-Tropsch wax and partly wax from the hydrogenation of brown coal.

iii. DETERGENTS (MERSOL)

In discussing the utilisation of the primary products of the Fischer-Tropsch process it was stated that most of the fraction 230–320°C was shipped to IG for conversion into detergent to supplement the meagre soap supplies. The product known as "Mersol" was prepared as follows:—

The Fischer-Tropsch oil containing 5–12% olefins was hydrogenated at 200–230ats using a nickel-tungsten sulphide catalyst and then treated with chlorine and SO_2 for 12–16hr in the presence of ultra-violet light. After removing HCl by blowing with air or nitrog n the product consisted of 82% sulphonyl chlorides an d 18% unreacted paraffins. This product, known as "Mersol D," was sent to soap manufacturers for saponification to the commerical product "Mersolat,"

TABLE LXI
PRODUCTS OF OXIDATION OF FISCHER-TROPSCH WAX

Fractions	Boiling range at 3–4mm	% of wax oxidised	Approximate carbon no.	Acid no.	Saponification no.	Unsaponified %
Forerunnings	up to 120°C	16	$<C_{10}$	450	451	nil
Main fraction	120–270°C	45	C_{10}–C_{20}	245	255	1·5
Higher fraction	270–315°C	10	C_{21}–C_{28}	155–160	175–180	10
Residue	>315°C	9	$>C_{28}$	80–90	110–120	?

The main fraction with the properties as shown above was converted into soap in the adjacent Märkische Seifen-Fabrik. The product was of excellent lathering properties but suffered from the disadvantage of leaving an unpleasant odour on the skin after use. For this reason, in the preparation of toilet soaps, not more than 30% of the total fatty acids used were synthetic.

For the preparation of acids for edible fat production a higher temperature (380°C) was used in the pipe still, and the raw acids before distillation had a lower ester number (acid no. 380, saponification no. 382). The fraction employed was similar in chain length to that us   for soap, i.e. C_8–C_{20}.

...e acids were esterified to the tri-glycerides with natural glycerine at 200°C and 2mm using 0·2% metallic tin as a catalyst. A 3–4% excess of acids over the theo-retical amount was used. The product was washed with alkali, treated with active charcoal and bleaching earth, and then steamed at 200°C and 2mm pressure. The refined fat was emulsified with 20% water, chilled and milled with the incorporation of carotene. This synthetic fat was officially approved as fit for human consumption by the Reichsgesundheitsamt (German Health Office), but

used mainly as a soap powder in admixture with water-glass or Tylose (a cellulose product). The product was believed to have a peace-time future for wool-washing and as an emulsifier in PVC and Buna rubber manu-facture.

The longer-chain Fischer-Tropsch soft wax would have been a superior raw material for this process but was not available in view of its use for fatty acid production as described above.

The IG plant at Leuna produced 50,000te/yr Mersol products from 35,000te/yr of Fischer-Tropsch oil. The oil was purchased at 30pfg/kg.

The power consumption for the UV irradiation was stated to be 0·002kwh/kg product.

iv. PROPYL AND BUTYL ALCOHOLS

In 1940, Rheinpreussen built a plant to produce propyl and butyl alcohols from the olefins present in the C_3 + C_4 fraction of the primary products of their Fischer-Tropsch plant. The process was as follows.

The C_3 + C_4 feed containing 30% olefins was mixed with 58°Bé sulphuric acid in a water-jacketed vessel

at a temperature not exceeding 45°C. After settling, the lower acid layer was removed and treated with water. The upper layer of polymers thus formed was separated and the lower layer containing the esters hydrolysed with steam in four stages. The dilute sulphuric acid was concentrated and returned to the esterification stage, and the distillate, consisting of a 50% aqueous solution of alcohols, treated in a series of six fractionating columns to produce pure isopropyl alcohol and a mixture of secondary and tertiary butyl alcohols.

The hydrocarbon layer from the esterification reactors was distilled, the unreacted C_3 and C_4 hydrocarbons recovered as bottled gas and the small amount of polymer residue, together with that obtained by treating the acid layer with water, was blended with motor fuel.

From a daily input of 26–28te of C_3-C_4 fraction, the production of isopropyl alcohol was 2·0–2·1te and of mixed butyl alcohols 3·2–3·5te.

During 1943 the production was as follows:—

Propyl alcohol	..	..	1,071·58te
Butyl alcohol	..	..	1,247·47te

4. RESEARCH AND DEVELOPMENT WORK

i. SYNTHESIS PROCESSES

a. Olefin Synthesis with Cobalt Catalyst

Although reference had been made in early publications of the Kaiser Wilhelm Institute to the possible advantages of recycling the residual gas in the Fischer-Tropsch synthesis, it was the Lurgi Gesellschaft who first demonstrated the advantages of the recycle method of operation. They showed that by recycling 2 to 3 parts of residual gas to each part of fresh gas in an otherwise normal medium pressure process with cobalt catalyst, the reaction proceeded more smoothly and was easier to control, the formation of methane and carbon was lower (despite the necessity of using a somewhat higher reaction temperature) and the proportion of olefins in the reaction products was higher.

Using this principle, Ruhrchemie developed their "olefin synthesis" to supply raw material for the OXO plant (see later) and synthetic lubricating oil plant. It was well known that use of gas mixtures richer in CO than normal synthesis gas led to increased olefin formation, but if water gas (H_2 : CO = 1·2 : 1) or gases even richer in CO were employed in the normal "straight-through" process, carbon was deposited on the catalyst. Ruhrchemie found, however, that if water gas is used as raw material and the end gas is recycled in the proportion of 3 parts to every part of water gas, carbon deposition is inhibited despite the fact that the mixed gas entering the reaction vessel has H_2 : CO ratio of about 1 : 1·2. Working at 10ats with temperatures in the range 200–220°C and with the normal cobalt catalyst, the olefin content of the spirit fraction was about 65% and that of the diesel oil fraction 40%. This process was very thoroughly studied by Ruhrchemie up to pilot-plant scale (one-tenth full scale) and preparations and alterations were almost complete at the end of 1944 to convert the whole of their medium pressure section to this method of working. The tail gas from the section was to be enriched with converted water gas to bring the H_2 : CO ratio to 2 : 1 and used as the feed gas for the two-stage atmospheric pressure section.

The proposed flow-scheme is shown diagrammatically in Fig. 53 and the characteristics of the process and its products are illustrated below by the results of a trial run carried out in 1941 in an experimental reaction vessel one twenty-seventh full scale, which lasted over 6 months.

Catalyst ..	..	..	Co 100 : ThO_2 5 : MgO 8 : kieselguhr 200
Raw material ..	..	water gas, H_2 : CO = 1·26:1, inerts = 14·0%
Reaction temperature	..	190–225°C
Period of running	..	204 days
Pressure ..	..	..	7ats gauge
Fresh gas input rate	..	30m³/hr (space velocity = 80)
Recycle ratio	..	..	3 : 1
Average gas contraction	59·3%
Average yields :	
Liquid hydrocarbons	121·8gm/m³ H_2 + CO :
„ „	+ C_3 and C_4: 131·7gm/m³ H_2 + CO
Methane formation, % of CO converted	..	6·6
CO_2 formation, % of CO converted..	..	..	2·2

FIGURE 53
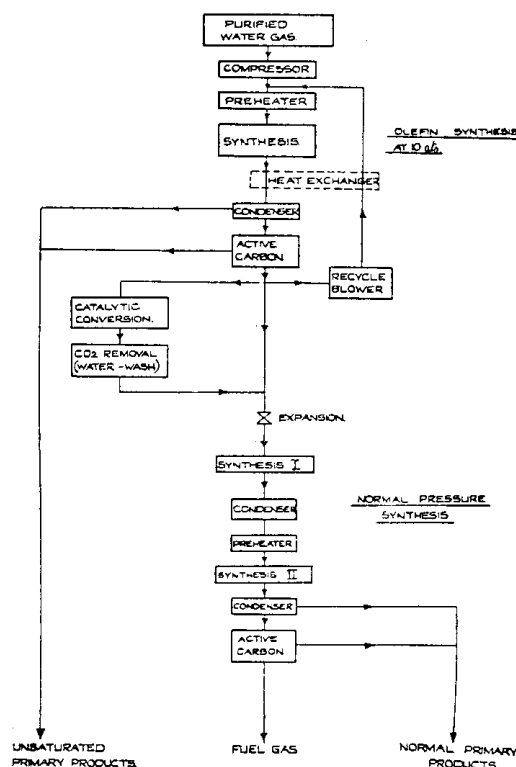
FLOW-SCHEME FOR OLEFIN SYNTHESIS FOLLOWED BY NORMAL PRESSURE SYNTHESIS

b. Composition of Product:

	% wt	Olefin content % vol
Spirit, <200°C ..	..	50	63
Oil, 200–320°C ..	..	25	45
Soft wax, 320–460°C	..	17	—
Hard wax, >460°C	..	8	—

The octane number (CFR Motor) of the spirit to 200°C varied between 40 and 44. After an "isomerisation-refining" process consisting of treatment in the vapour phase over activated clay ("Floridin") at 300°C, the octane number was increased to 60–66. The primary spirit was a suitable raw material for lubricating oil synthesis by the aluminium chloride process, and gave

a 48% weight yield of oil of viscosity at 50°C = 17·0°E and of viscosity index ca.115.

The use of recycling increases the power consumption and hence the cost of the process, but from the point of view of Ruhrchemie this was justified by the increased value to them of the olefin-rich products obtained.

c. Dry Regeneration of Cobalt Catalyst

Ruhrchemie have found that at the end of the normal life period (4–8 months) in synthesis at atmospheric pressure, the cobalt catalyst can be completely reactivated by treatment with hydrogen at about 400°C under the conditions used in the initial reduction. The action of this "dry regeneration" process, as it was called, was said to be the removal of carbon and high molecular-weight substances not removed by the normal solvent and low-temperature hydrogen treatment. In small-scale experiments the activity of the catalyst had been maintained for 2 years by the use of this procedure.

Although all this had been discovered in 1939–1940, no attempt was made to put it into practice on the full scale. The main reason for this appeared to be that Ruhrchemie and other owners of catalyst factories were loth to lose the money they had invested in plant built on the basis of a catalyst life of 4 to 6 months.

d. The Use of Iron Catalysts

Fischer's pioneer work on the synthesis process was carried out mainly with catalysts containing iron as the active component, and although cobalt was ultimately adopted as the catalyst for large-scale operation in view of its higher activity and lower temperature of operation, research on the use of iron catalysts has continued without a break up to the present day.

The outbreak of war, which restricted and later stopped the importation of cobalt, caused an intensification of research on iron catalysts, first with a view to using them in any new plants erected, and later, when the cobalt situation became more acute, in order to replace cobalt in existing plants. Research was proceeding in six different organisations (whose work is summarised below) each developing what they regarded as the most suitable iron catalyst. In order to decide which of these was the most promising for application on the large scale, the Reichsamt für Wirtschaftsausbau (Office for Economic Development) arranged for simultaneous trials of six different iron catalysts at the Brabag (Schwarzheide) works in the winter 1943–1944. A summary of the results of these trials is given later. The Reichsamt does not appear to have come to any conclusions as to which catalyst was the most satisfactory, and it is not easy to come to any very definite conclusion except that none of them equalled the performance of the standard cobalt catalyst.

The possible variations in process conditions and products obtainable are very great in the case of iron catalysts. By variation in catalyst composition, method of preparation, method of reduction, composition of synthesis gas and process conditions, the course of the reaction can be altered within wide limits. The reaction products may consist largely of the low-boiling hydro-carbons or contain over 50% of hard wax. The olefin content can range from 30 to 80%, and the alcohol content from 2 to 60%. In contrast to the reaction with cobalt catalysts, where hydrogen and carbon monoxide always react in the proportions 2·0–2·3 : 1, with iron catalysts the ratio can vary from 0·5 : 1 to 2·0 : 1 according to the extent to which CO_2 or H_2O appears as the oxygen-containing product.

This extreme flexibility of the iron-catalysed process

has the disadvantage of introducing difficulties in reproducibility of catalyst performance, and despite the amount of research work carried out it would appear that no iron-catalyst process developed in Germany had reached the stage where it could be put into operation on the industrial scale and be expected to work as smoothly and efficiently as the cobalt-catalyst process.

The work of the various organisations is briefly reviewed below.

e. Ruhrchemie AG

This Company prepared over 2,000 trial batches of iron catalyst and carried out experiments on a scale varying from 50ml to 1,000 litres catalyst (one-tenth full scale). Their studies were confined to the conventional precipitated type of catalyst, usually containing— in addition to iron—copper, an activator often CaO, and kieselguhr. They favoured reduction of the catalyst in hydrogen before use and the use of recirculation of residual gas in the synthesis. Up to the end of 1942 they were not particularly concerned to restrict the temperature and pressure of operation to the limits imposed by existing synthesis vessels and they developed a process to operate at 240–260°C and 20ats which they successfully "sold" to an Italian concern (Società Italiana Carburanti Sintetici). This firm commenced the erection of a plant to operate this process at San Giovanni Valdarno, but had not got beyond site preparation when the war with Italy ended.

The characteristics of the process were as follows.

Catalyst.—Fe 100 : Cu 5 : CaO 10 : kieselguhr 150, prepared by rapid precipitation from the nitrates with potassium hydroxide at the boiling point, and reduced in dry hydrogen for about 1hr at 300°C. Bulk density: 0·404.

Process conditions and results (data from single-stage experimental run at one-tenth full scale):

Raw material	..	water gas H_2 : CO = 1·27 : 1, inerts = 13·7%
Temperature	..	251–257°C
Pressure	..	20ats (gauge)
Recycle ratio	..	Fresh gas 1 : residual gas 2·5
Gas throughput	..	98m³/hr water gas, space velocity ca.90/hr

Results (average figures for 120 days running):

Gas contraction	..	..	52·0%
Yield of liquid and solid hydrocarbons	..	..	103·0gm/m³ H_2 + CO
Yield of C_3 and C_4 hydrocarbons			13·5gm/m³ H_2 + CO
Production of C_1 and C_2 hydrocarbons	..	..	11·0% CO converted
Production of CO_2	..	..	26·8% „ „
Utilisation ratio H_2 : CO	..		1·23 : 1

Composition of product:

Spirit, 60–200°C	..	46%wt olefins : 66 vol %, OH no. 24
Oil, 200–320°C	..	18% wt olefins : 52 vol %
Soft wax, 320–460°C	..	19% wt
Hard wax, >460°C	..	17% wt

Polymerisation of the spirit with aluminium chloride, after removal of alcohols by zinc chloride treatment, gave a yield of 46·6% lubricating oil of viscosity 9°E at 50°C and viscosity index ca.115. It will be noted that hydrogen and carbon monoxide reacted in approximately the same proportions as present in water gas. One of the main factors contributing to this desirable result was the use of recirculation.

Ruhrchemie guaranteed that their Italian licensees would obtain a yield of 140gm primary products (including C_3 and C_4) per m³ inert-free water gas by working in two stages and changing the catalyst every 4 months. They estimated the cost of the fresh, reduced catalyst

at RM2·38/te or RM9,500 per reaction vessel charge, and the catalyst cost at 3·7pfg/kg total primary products for a catalyst life of 4 months. These figures are higher than the corresponding ones for cobalt catalyst, due mainly to the cost of the potassium hydroxide and nitric acid used. They could be reduced somewhat by recovery of potassium nitrate from the mother liquor and wash waters.

The form of reaction vessel suggested for this process was the normal double-tube type used for medium pressure synthesis but constructed to stand 25ats gas pressure and 50ats steam pressure.

From the end of 1942 onwards Ruhrchemie concentrated on the development of an iron catalyst which could be used in existing reaction vessels, *i.e.* one which would operate satisfactorily at 10ats and at temperatures not greater than 225°C. The catalyst of this type used by Ruhrchemie in the Reichsamt comparison experiment at Ruhland-Schwarzheide contained ceria in place of calcium oxide as promoter, but their most promising "low-temperature" iron catalyst (discovered after these experiments) was, apart from kieselguhr content, similar in composition to the earlier high-temperature catalyst. The composition was Fe 100 : Cu 5 : CaO 10 : kieselguhr 30, prepared by precipitation from the nitrates with sodium carbonate solution at the boiling point and impregnated, after filtering and washing, with 3% KOH (based on iron content).

The performance of this catalyst (after reduction in hydrogen at 300°C for 1hr) in a reaction vessel of 5 litres catalyst capacity is indicated by the following data:—

Reaction conditions over 5 months' operation:

Raw material	..	water gas
Temperature	..	200–220°C
Pressure	..	10ats
Recirculation ratio	..	1 part water gas : 2·2 parts residual gas
Gas throughput	..	500 litres/hr (space velocity : 100/hr)

Average results:			*For 1st month*	*For 5th month*
Yield of hydrocarbons higher than C₁, gm/m³ H₂ + CO	..	..	121·5	118·3
Methane formed, % CO converted			3·6	4·7
Utilisation ratio H₂ : CO	..	..	1·04 : 1	1·12 : 1

Composition of product:			% wt	% wt
Spirit, 60–200°C	..	..	16·5	25·1
Oil, 200–320°C	..	..	15·9	17·8
Soft wax, 320–460°C	..	..	27·9	25·5
Hard wax, >460°C	..	..	39·7	31·6

Certain iron catalysts of similar composition to the above, but reduced under different conditions, were found to give products containing up to 60% of alcohols, the alcohols being distributed throughout the boiling range of the product.

f. Kaiser Wilhelm Institute (Mülheim)

The characteristic features of the work in this organisation were the use of catalysts containing no carrier or support and consisting only of iron, copper and a little alkali (potassium salt) and the pretreatment of the catalyst in CO or gases containing CO in preference to reduction in hydrogen. In further contrast to Ruhrchemie they had paid little attention to developing catalyst specifically adapted to utilising hydrogen and carbon monoxide in the proportions found in water gas and had carried out many experiments using gas with an H₂ : CO ratio of 2 : 3, *i.e.* the proportions in which the gases react in the presence of the majority of iron catalysts when there is no residual gas recirculation.

The Institute regarded the pretreatment of the catalyst as being of greater importance than the composition and the latter was more or less fixed at Fe 100 : Cu 1–3 : K₂CO₃ 0·5–1. It was prepared by rapid precipitation of the nitrates (or preferably a mixture of ferric nitrate, ferrous chloride and cupric nitrate) at the boiling point with potassium carbonate solution, washing free from alkali salts and then adding the required amount of potassium carbonate solution, drying and granulating.

The recommended pretreatment consisted in passing 25 litres/hr pure CO for each 10gm Fe for 4hr at 325°C and at 0·1ats absolute pressure or passing water gas at 4 litres/hr per 10gm Fe for 2 to 3 days at 240–250°C and at atmospheric pressure. This treatment causes the formation of Fe₃C which is claimed to be the active form of the catalyst.

The highest conversions were obtained at 20ats with synthesis gas of H₂ : CO ratio 2 : 3. Under such conditions an average yield of 120gm of hydrocarbons higher than methane per m³ of synthesis gas was maintained for a year using a temperature of 235°C. It was admitted that, owing to carbon deposition when using gas rich in CO, inclined tubes with a free space above the catalyst to allow for expansion had to be employed and that for technical operation it would be preferable to employ water gas.

The performance of the KWI catalyst with water gas is indicated by the data for the Reichsamt comparison experiment given later.

The Ruhrchemie criticised the KWI type of catalyst on the grounds that iron catalysts containing no kieselguhr would present grave difficulties in filtration when prepared on the large scale, that such catalysts were not mechanically robust and that they gave an uneconomically high content of iron per reaction vessel.

g. IG Farbenindustrie AG

The work of this organisation appears to have been influenced little, if at all, by the work of the KWI or Ruhrchemie and has followed the line originated by the Badische Anilin und Soda Fabrik using pure sintered iron plus a little alkali as the basis of their catalysts. A number of different processes were developed and are briefly described below.

(i) *Fixed-bed, circulating-gas process.*—In this process the "traditional" method of heat dissipation by use of a multiplicity of cooling tubes and surfaces is discarded and the heat of reaction is removed in the gas stream by recirculating 100 volumes of residual gas for every volume of fresh gas introduced, the catalyst being arranged in a shallow, wide bed (*e.g.* 1·0m deep by 1·5m diameter).

The catalyst was prepared by pasting iron powder, obtained by thermal decomposition of iron carbonyl, with 1% of borax and then sintering and reducing by heating in hydrogen at 800–850°C for 4hr.

Process conditions:

Synthesis gas	..	H₂ : CO ca.1·25 : 1, S <0·2gm/100m³
Temperature	..	ca.325°C
Pressure	..	20ats
Contact time	..	0·5–1sec
Recycle ratio	..	100 : 1

Products: % wt

Ethylene + C₃ + C₄	..	30
Spirit, <200°C	..	48 (7% alcohols, olefins 70%)
Gas oil	..	14 (4% alcohols)
Wax	..	1
Alcohols from reaction water	..	7 (mainly C₂)

The output of the above products was 700–800kg/day per m^3 catalyst. For every 100kg of these products, 25kg of methane and ethane were produced.

The crude spirit had an octane number of 68–70 (Research) and after treatment with alumina at 400–450°C and fuller's earth at 180–200°C, with a loss of 5%, the _octane number was 84 (Research), 75–78 (Motor).

The process had been operated successfully over a period of 10 months on a scale of 5 litres catalyst but larger-scale experiments had not been so successful, due either to turbulence or channelling, both of which lead to local overheating of the catalyst.

Disadvantages of this process are the high power requirements for the recycle and the difficulties and costs of condensing out products from large volumes of circulating gas. Cost estimates made by IG for this process compared unfavourably with those for the Ruhr-chemie cobalt catalyst process, and it appears that the development of this process had been discontinued in recent years.

(ii) *The foam process.*—The object of this process was to produce olefins boiling in the gas oil range for use in chemical synthesis. The catalyst was prepared by pasting carbonyl iron with potassium carbonate or borate, drying, and reducing in hydrogen at 350–450°C. The reduced catalyst was ground to a fine powder in a ball mill in the presence of gas oil, and the reaction was carried out by forcing water gas through a ceramic plate at the base of a cylindrical vessel containing a suspension of the catalyst in a high-boiling fraction of synthetic oil.

Process conditions:

Temperature	..	..	250°C
Pressure	..	..	20ats
Time of contact	..	..	ca.3min

Products: % *wt*

C$_3$ + C$_4$	..	..	10
Spirit, <200°C	..	..	40–50 (70% olefins)
Oil, 200–350°C	..	..	30 (40–50% olefins)
Wax ..	..	..	20–25

The output of these products was 350–450kg/day per m^3 reaction space. In addition, 5–10kg methane was produced per 100kg of "useful" products.

This process was tried out on a scale of 1·5m^3 reaction space.

(iii) *Conventional tubular reactor process.*—This process utilised the normal type of tubular reactor with water cooling, but employed the sintered type of catalyst favoured by IG. The catalyst was prepared by mixing iron oxide with 5–25% MgO or MgCO$_3$ and 1–2% potassium carbonate or borate, pelleting and then sintering by heating to 850°C in nitrogen, cooling and then reducing in hydrogen at 350–450°C.

Process conditions:

Synthesis gas	..	H$_2$: CO = 1·25 : 1 to 0·8 : 1
Temperature	..	230–250°C
Pressure ..	..	20ats

Products:

C$_3$ + C$_4$	..	10% (olefins 70%)
Spirit, < 200°C	..	35–50% (olefins 70%, oxygen 4–6%)
Oil, 200–350°C	..	25–35% (olefins 40–50%, oxygen 3–5%)
Wax >350°C	..	15–25%
Output of above products	..	350–450kg/day per m^3 catalyst space
Methane production		10kg/100kg "useful" products

This process was tested out over a period of several months in a reaction vessel of 20 litres catalyst capacity.

It is probable (though it is not known definitely) that the catalyst used in this process was the one employed by IG in the Reichsamt comparative experiments reported later.

(iv) *Fixed bed, circulating oil process.*—In this process the same catalyst as that employed in the preceding process (iii) was used but in place of external water-cooling, the heat of reaction was removed by circulating oil through the catalyst bed.

Process conditions:

Synthesis gas	..	H$_2$: CO = 0·82 : 1
Temperature	..	260–300°C in Stage I, 280–330°C in Stage II
Pressure ..	..	20–25ats
Gas throughput	..	Controlled to give 20–25gm/hr products per litre catalyst
Conversion	..	ca.150gm useful products/m^3 H$_2$ + CO

Products: % *wt*

C$_3$ + C$_4$	..	16 (85% olefins)
Spirit, < 200°C	..	40 (50% „)
Oil ..	..	20 (25% „)
Wax	..	20
Alcohols (C$_1$ + C$_2$)		4

The spirit contained 1% oxygen and had a Research octane number of 62–65. The process had been operated for a long period in a pilot plant with an output of 8–10te/month.

(v) *The "Synol" process.*—This process was designed for the production of straight-chain primary alcohols for use as chemical intermediates. The catalyst was prepared by melting iron in a blast of oxygen and incorporating aluminium nitrate and potassium nitrate in the melt so that the finished product contained 2% Al$_2$O$_3$ and 1% K$_2$O based on iron content. It was identical with that used by the IG for ammonia synthesis and was reduced in hydrogen at 450°C before use.

Process conditions:

Synthesis gas..	..	H$_2$: CO = 0·75 : 1
Temperature	..	185 rising to 200 or 225°C after 9 months
Pressure ..	..	18–20ats
Space velocity	..	100–150
Recycle ratio..	..	50 : 1

By using two stages in series a yield of 155–165gm of liquid products per m^3 H$_2$ + CO was obtained.

Products: Fraction	% wt of total	% wt alcohols	% wt paraffins	% wt olefins
Up to 150°C	} 70	{ 20	40	40
150–200°C		{ 70	15	15
200–300°C	} 30	{ 50	20	30
> 300°C		{ 30	42	28

The alcohols were separated by means of their boric acid esters.

The reaction was tried out in both tubular and plate-type reactors using diphenyl as cooling medium but difficulty had been experienced in removing the spent catalyst from both types. The process had been operated on a scale of 3 to 5te/month liquid products.

h. Lurgi Gesellschaft für Wärmetechnik

The best iron catalyst developed by this Company in their Frankfurt-am-Main laboratories was stated to have the composition Fe 100 : Cu 25 : Al$_2$O$_3$ 9 : K$_2$O 2 : kieselguhr 30. It was prepared by precipitation from the nitrates with sodium carbonate solution at the boiling point, filtering and washing the cake and then adding the requisite amount of alkali as K$_2$CO$_3$. Reduction in hydrogen at 250–350°C for 1–4hr was carried out before

use. The catalyst was designed for use in conventional-type reaction vessels in a two-stage process using water gas as raw material and employing a 2·5 : 1 recycle in Stage I.

Process conditions:

Pressure	..	20ats
Temperature	..	220–230°C (over 3 months)
Space velocity	..	100m³/hr water gas per m³ catalyst
Yield in Stage I	..	136gm C_3 and higher hydrocarbons per m³ H_2 + CO
Yields for 2 Stages	..	C_1 + C_2 : 18gm/m³ H_2 + CO
		C_3 + C_4 : 15gm/m³ H_2 + CO
		C_5 and above : 146gm/m³ H_2 + CO
		Alcohols : 9gm/m³ H_2 + CO

Products:		% wt
Spirit,	..	20 (olefins 60%)
Oil, 200–320°C	..	20 („ 45%)
Soft wax, 320–460°C		15
Hard wax, >460°C	..	45

The Company considered the high proportion of hard wax obtained in this process a particularly advantageous feature, owing to the high price fetched by this material.

It seems likely that the above catalyst was used by Lurgi in their Reichsamt test reported later.

Lurgi had also developed a process primarily intended for the detoxification of town gas produced by the Lurgi pressure-gasification process, but which also produced some synthetic oil. This process used a precipitated iron catalyst of composition Fe 100 : Cu 5 : Al_2O_3 9 : kieselguhr 120 at a temperature of 250°C and a pressure of 20ats in a single stage without recirculation. A pilot plant had been erected at the AG Sächsische Werke, Böhlen, near Leipzig, but only a few short runs had been carried out. This unit consisted of a normal Fischer-Tropsch tube-and-plate type assembly enclosed in a cylindrical shell and held about 6m³ of catalyst. Lurgi gas, of CV = 4,200k.cal/m³ and containing 17% CO was purified from sulphur compounds and passed through the unit at 1,600m³/hr. The exit gas, amounting to 1,200m³/hr, contained 5–8% CO and had a CV of 4,300k.cal/m³. About 30–40gm of liquid products per m³ input gas were recovered by the usual methods of condensation and absorption. The composition of this product was as follows:—

		% wt
Spirit ..	.. ..	25–30 (olefins 50–60%)
Middle oil	.. ..	10–30
Soft wax	.. ..	20–30
Hard wax	.. ..	25–30

i. Rheinpreussen

This Company had carried out laboratory research on precipitated iron catalysts containing copper and alkali with magnesia as activator, and dolomite or kieselguhr as support. As a result of studies of carbide formation they had concluded (like the KWI) that pretreatment of the catalyst with a low partial pressure of CO was preferable to reduction in hydrogen. They found that a recycle ratio of 10 : 1 gave optimum results and claimed yields as high as 150gm C_2 and higher hydrocarbons per m³ inert-free gas for single-stage operation at 10ats and 200–220°C. One sample of catalyst had been maintained in operation for 3½ years and was still giving a yield of 130gm C_2 and higher hydrocarbons per m³ at the end of that period.

This organisation appears to be alone in having achieved considerable success in the development of an iron catalyst suitable for atmospheric pressure operation. Thus, for example, a catalyst of composition Fe 100 : Cu 10 : Mg 20 : kieselguhr 50 : K_2CO_3 2, gave a yield

of 135gm C_2 and higher hydrocarbons per m³ H_2 + CO in one stage at atmospheric pressure and 200–220°C using synthesis gas (H_2 : CO = 2 : 1) and recirculating 10 parts of dried CO_2-free residual gas to each part of fresh gas introduced.

Rheinpreussen had also studied the use of iron catalysts in the liquid phase and obtained very promising results.

A complete account of this Company's researches on iron-catalyst development has not yet been obtained.

j. Brabag

Comparatively little is known of this Company's work on iron catalysts. They appear to have worked mainly on catalysts operating at high temperatures (250–270°C) with CO-rich gas (H_2 : CO ca.0·6 : 1) at 10–15ats. They had developed promising catalysts consisting of "Lauta-masse" and alkali carbonates which were little more than refinements of the normal organic sulphur purification material. One such preparation containing 5–6% K_2CO_3 gave an average yield of 146gm C_2 and higher hydrocarbons per m³ H_2 + CO at 246°C over a period of 3 months. The products contained 70–80% of olefins and the octane number (Research) of the spirit-fraction (38–160°C) was claimed to be 82.

k. The "Reichsamt" Comparative Experiments

The trials of six different iron catalysts were carried out in 5-litre catalyst vessels at the Ruhland-Schwarzheide works of Brabag, and started in September, 1943. The conditions laid down were as follows:—

Synthesis gas..	..	Water-gas
Temperature	..	Not to exceed 225°C
Pressure	..	10ats
Recycle	..	None
Duration of test	..	Three months (without change of catalyst)
Products	..	Must resemble those obtained with cobalt catalyst sufficiently to be marketable as substitutes

The experimental data and results are summarised in Table LXII.

The operating conditions were practically identical in all cases and hence the observed variations in the course of the reaction and the yield and nature of the products must be attributed solely to differences between the catalysts.

The characteristics required for successful operation on the large scale (apart from questions concerning the composition of the liquid products) were a high degree of conversion to non-gaseous products with a low degree of gas production—particularly of methane—an H_2 : CO utilisation ratio closely approaching the H_2 : CO ratio of the process gas (to enable further stages of synthesis to be operated satisfactorily) and a high yield of desired products per unit weight of catalyst.

It will be observed that none of the catalysts tested combined all these desirable features and the order of merit in which the catalysts are placed depends on the particular feature used as criterion.

It is also clear that catalysts for large-scale use must be reasonably consistent in behaviour and it is important to note that in the above tests only the Lurgi, IG and Ruhrchemie catalysts behaved satisfactorily at the first attempt. In the case of KWI, Brabag and Rhein-preussen, the observed results were only obtained at the second, third and fourth attempts respectively.

l. The "Iso-synthesis"

A characteristic feature of the products of the Fischer-Tropsch synthesis with cobalt or iron catalysts is their

TABLE LXII

DATA FOR REICHSAMT TESTS OF SIX IRON CATALYSTS

Pressure 10ats
Raw material .. .. Water gas containing 12% inerts
Method of operation .. Single-stage without recirculation
Period of test .. 90 days

Reaction vessel No.	1	2	3	4	5	6
Organisation supplying catalyst	KWI	Lurgi	Brabag	IG	Ruhr-chemie	Rhein-preussen
Catalyst volume.. .. .. litres	4·8	4·8	4·8	4·8	4·8	4·8
,, weight .. .. kg	4·9	3·79	6·08	10·9	2·1	3·28
Reaction temperature .. .. °C	195–224	188–220	219–225	163–220	186–222	190–224
Space velocity .. .. vols gas/vol cat space/hr	108·7	106·9	110·7	115·0	103·8	104·0
Gas contraction .. .. %	42·7	39·1	36·4	38·5	33·0	39·2
H_2 + CO converted .. .. .. %	69·3	64·8	58·2	63·1	54·2	57·2
Yield of hydrocarbons, excluding CH_4 gm/m³ water gas	112·2	112·2	102·7	105·8	92·8	94·2
,, CH_4 .. .. ,, ,,	9·9	6·4	3·0	7·8	5·5	7·9
,, oxygen in primary products ,, ,,	3·1	5·9	2·7	3·5	4·8	1·9
H_2 utilisation .. .. moles per mole of CO	0·80	0·66	0·69	0·74	0·72	1·07
Composition of total products :						
Gases C_1 and C_2 .. .. .. % wt	16·6	10·8	8·4	16·8	13·6	17·1
,, C_3 and C_4 .. .. .. ,,	19·9	12·3	9·8	18·1	14·3	21·5
Spirit C_5–C_{10} .. .. .. ,,	25·1	19·5	17·9	25·7	22·3	29·8
Diesel oil C_{11}–C_{18} .. .. .. ,,	14·0	13·1	16·4	11·5	12·7	13·7
Soft wax, 320–450°C.. .. .. ,,	7·9	8·2	12·6	6·1	7·1	6·3
Hard wax, >450°C .. .. .. ,,	10·3	27·0	30·8	14·8	18·7	6·3
Low-boiling alcohols .. .. ,,	6·2	9·1	4·1	7·0	11·3	5·3
	100·0	100·0	100·0	100·0	100·0	100·0
Total alcohols .. .. .. ,,	7·0	14·4	9·5	10·7	15·8	7·5
,, esters .. .. ,,	1·1	8·0	2·7	1·7	2·6	0·3
,, olefins .. .. .. ,,	25·9	30·4	34·2	39·1	26·1	29·7

CATALYST DATA

KWI.—Composition—Fe 100 : Cu 1 : K_2CO_3 1 by precipitation from nitrates. Reduced in synthesis gas H_2 : CO = 2 : 1 at 325°C and 0·1ats (absolute) for 24 hours.

Lurgi.—Composition—Fe 100 : Cu 10 : SiO_2 30 : K_2O 2. Reduced in hydrogen at 250–350°C.

Brabag.—Composition (by Ruhrchemie analysis)—Fe 100 : Cu 20 : Zn 20 : K_2CO_3 1. Pretreated in water gas at 235–240°C for 48 hours.

IG.—A sintered iron catalyst containing Al_2O_3 and K_2O and using calcium fluoride as support.

Ruhrchemie.—Composition—Fe 100 : Cu 5 : CeO_2 10 : kieselguhr 50 by precipitation from nitrates. Reduced in hydrogen at 300°C.

Rheinpreussen.—Composition—Fe 100 : Cu 5 : $CaCO_3$ 100 : K_2CO_3 0·5–1·0. Reduced in water gas at 240–250°C, atmospheric pressure.

predominantly straight-chain character. Work during the war years at the Kaiser Wilhelm Institute, Mülheim, however, resulted in the development of a process for producing predominantly branched-chain hydrocarbons —mainly isobutane.

The reaction conditions required for this process are a temperature of 450°C, a pressure of 300ats and the use of oxide catalysts such as thoria alone, thoria and alumina, or zinc oxide and either thoria, alumina, ceria or zirconia. The gas mixture used has a ratio H_2 : CO = 0·88 : 1 and does not require purification from sulphur compounds. The space velocity is much higher than in the normal Fischer-Tropsch process and is in the region of 1,000/hr. Although the reaction is not so sensitive to temperature as the normal synthesis, com-

paratively narrow tubes (20–25mm internal diameter) are used and means of cooling must be provided. The tubes must be constructed of high alloy steel or must be lined with copper to prevent formation of iron carbonyl. The yields obtained with various catalysts are shown below.

The liquid hydrocarbons consist mainly of isopentane and branched-chain hexanes with smaller amounts of higher hydrocarbons, including naphthenes. By using higher temperatures, aromatic and naphthenic hydrocarbons appear in greater amounts, but the main product is methane. At lower temperatures, alcohols predominate and the mechanism of formation of isobutane is believed to be via the intermediate formation of isobutyl alcohol and isobutylene.

TABLE LXIII

"ISO-SYNTHESIS" RESULTS

Catalyst	% CO converted	Yield in gm/m³ H_2 + CO						
		Liquid H/C	Alcohols	iso-C_4	n-C_4	C_3	C_2	C_1
ThO_2	62	42	20	23	3	11	4	11
ThO_2 + 0·6% K_2CO_3	62	65	26	12	1	2	1	6
ThO_2 + 20% Al_2O_3 + 3% K_2CO_3 (based on Al_2O_3)	78	25	0	85	10	0	7	22
ZnO + Al_2O_3 (equimolar)	—	24	8	50	6	10	—	—

The catalyst is prepared by rapid precipitation from the nitrate with sodium carbonate at the boiling point and after drying is heated in air to 300°C for 2–3hr before use. This treatment is repeated at intervals (*e.g.* three times in 4–5 months) to regenerate the catalyst by removal of carbon deposits.

This process had never been tested on a scale greater than that in the laboratory (20gm catalyst).

m. The Synthesis of High Melting point Waxes

The synthesis of hydrocarbon wax from hydrogen and carbon monoxide in the presence of ruthenium catalysts, which was studied on the laboratory scale at the Kaiser Wilhelm Institute, has been fully described in the technical literature and no advances appear to have been made since the appearance of the last paper (Brennstoff-Chemie, 1940, 21, 273). The catalyst used was ruthenium dioxide obtained from potassium ruthenate, and the operating conditions were:—

Synthesis gas.. .. $H_2 : CO = 2 : 1$
Temperature .. 195°C
Pressure 100ats
Gas rate .. .. 1 litre/hr per/gm Ru

The yield obtained in one stage was 150–160gm/m³ H_2 + CO, and 65% of the product was pure white wax melting at 118–120°C. By solvent extraction wax melting at 130°C could be separated. The catalyst life appeared to be extremely long, the yield falling by only 10% after 18 months operation. It was, however, necessary to purify the synthesis gas from sulphur compounds even more rigorously than is usual with cobalt catalysts.

The formation of methane is extremely small and, in fact, the only hindrance to the further development of this process is the scarcity of ruthenium.

ii. SECONDARY PRODUCTS

a. The OXO Synthesis

Research work in the laboratories of Ruhrchemie resulted in the discovery of a new reaction of fairly general applicability. It was found that olefins will react with hydrogen and carbon monoxide in the presence of cobalt catalysts in the liquid phase at temperatures in the range 110–150°C and pressures of the order of 150ats to form the aldehyde one carbon atom greater in chain length, and that the aldehyde can then be hydrogenated under similar conditions with the same catalyst to give the corresponding alcohol.

Although this reaction can be entirely divorced from the products of the Fischer-Tropsch synthesis and process conditions were worked out for the production of propyl aldehyde from ethylene, the main German interest in the process was for the production of C_{12} to C_{18} alcohols for conversion into their sulphate esters for use as detergents. For this purpose, long-chain olefins produced either directly by the Ruhrchemie olefin synthesis (Section D4 (i.) *a.*) or by the mild thermal cracking of Fischer-Tropsch wax would be used as raw material.

To operate this process a company known as the OXO-Gesellschaft was formed by Ruhrchemie in association with IG and Henkel et Cie. A plant was built at Holten to produce 12,000te/yr alcohols and was almost ready to go into production when the works of Ruhrchemie were put out of action by bombing at the end of 1944.

The process, which was to be operated batch-wise, is illustrated in the diagrammatic flowsheet, Fig. 54.

The feed material containing 40–50% olefins is cut into four fractions: C_{11}–C_{12}, C_{13}–C_{14}, C_{15}–C_{18} and C_{17} (to facilitate subsequent separation of the alcohols), each of which is treated separately. The OXO reactors (12m high by 40cm internal diameter, fitted with internal water-cooling tubes) are charged with 700 litres of liquid feed, containing in suspension 3–5% of finely-ground reduced Fischer-Tropsch cobalt catalyst, and water gas is recirculated through the reactor at 200m³/hr. A temperature of 135°C and a gas pressure of 150ats are maintained in the reactor. The reaction is complete in 20–30min, when the contents of the reactor are transferred to the hydrogenation vessel (of identical size and construction) and hydrogen is recirculated through the suspension at a temperature of 180°C and at 150ats. During the OXO reaction, cobalt carbonyl goes into solution and becomes decomposed in the hydrogenation stage. The liberated CO is removed from the recycle hydrogen by conversion to methane over an iron catalyst.

FIGURE 54
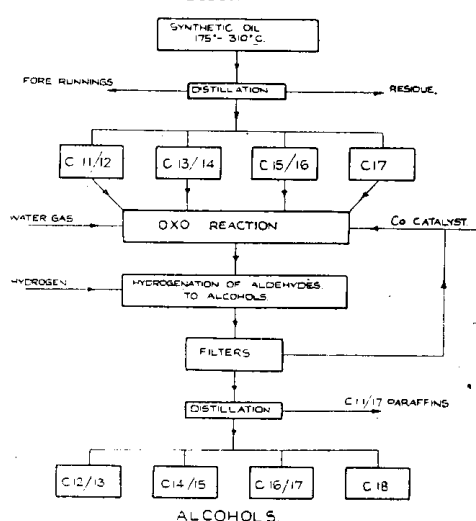
FLOW-SCHEME FOR OXO SYNTHESIS

The Fischer-Tropsch cobalt catalyst was used only because of its availability; the true catalyst is cobalt carbonyl and any suitable source of this compound can be used.

The product from the hydrogenation stage is then filtered through ceramic thimbles and the recovered catalyst used together with fresh feed material for the next batch. The filtered product is distilled under reduced pressure to yield alcohols of 98% purity, unreacted hydrocarbons and 5–15% (based on the alcohols) of heavy oil consisting of ketones, condensed aldehydes and hydrocarbons. The unreacted hydrocarbons were to be returned to Ruhrchemie as diesel oil.

The alcohols are all primary, but are mixtures of isomers.

IG had worked out a continous process operating under similar conditions, but permitting a throughput 9–10 times greater than the Ruhrchemie batch process for the same degree of conversion (95% reaction). This process had been operated on a pilot-plant scale with an output of 40–50te/month alcohols.

Costs.—The estimated costs for the OXO plant at Holten, based on the operation of a one-tenth scale pilot-plant, are given in Table LXIV.

TABLE LXIV

COSTS FOR A PRODUCTION OF 12,000TE/YR OXO ALCOHOLS

Materials:—		RM
Ruhrchemie olefins 12,000te at RM0·4/kg	..	4,800,000
Water gas at 10ats (from Ruhrchemie) 6,000,000 m³ at RM0·04/m³	.. ..	240,000
Hydrogen at 10ats (from Ruhrchemie) 3,000,000 m³ at RM0·075/m³	.. ..	225,000
		5,265,000

Wages and salaries:—		
150 men, 8hr/day, 365 days at RM1·10/hr	..	481,800

Energy:		
Steam: 78,000te, 80ats at RM4·00/te	.. ..	312,000
97,000te, 18ats at RM3·50/te	.. ..	339,000
100,000te, 2·5ats at RM2·55/te	.. ..	255,000
Electricity: 10,160,000kwh at RM0·03/kwh	..	304,800
Water: 1,344,000m³ at RM0·075/m³	.. ..	100,800

Accessory materials:—		
Catalyst	.. ..	72,000
Lubricating oil, etc	.. ..	24,000

Repairs and maintenance:—		
4% of plant cost (RM11,000,000)	.. ..	440,000

Other costs:—		
Transport, insurance, etc	.. .. ..	18,000
Laboratory costs (25% of wages and salaries)	..	120,450
General expenses, including management (40% of wages and salaries)	.. ..	192,720
Total	.. ..	7,926,070

Capital charges:—		
Interest and depreciation, 13·5% of capital cost (RM11,000,000)	.. ..	1,485,000
Taxes	.. ..	120,000
Total	.. ..	9,531,000
Less Credit for by-product	.. .. ..	144,000
Total production cost	.. .. ..	9,387,070

i.e. 78·23pfg/kg alcohols.

IG estimated that the cost would be 60pfg/kg, using their continuous process.

Olefins obtained from Fischer-Tropsch sources were considered to be by far the most suitable raw material for the process. Olefins derived from the cracking of petroleum could be employed, but it was considered desirable in this case to separate them from non-olefinic material before use.

The conditions necessary for the manufacture of propyl aldehyde from ethylene had been worked out by Ruhrchemie and are illustrated by the following example.

A suspension of 5 litres Fischer-Tropsch cobalt catalyst in 30kg toluene was placed in a vertical tubular reactor of 90 litres capacity. The pressure was raised to 150ats, using water gas, the temperature held at 115°C, and a mixture of 25% ethylene, 35% H_2 and 25% CO passed through at 18m³/hr. Conversion of ethylene was 100% during a period of 165min, by which time the volume of liquid had increased by nearly three times and the reaction was stopped. The liquid was then allowed to settle, the catalyst removed by filtration, and the filtrate fractionated. The products, based on the raw materials consumed, were as follows:—

Propyl aldehyde	.. ..	70–80%
Ethane, methyl ethyl acrolein and diethyl ketone	.. ..	15%
Loss ..	.. ..	5%

The distillation residue after distilling off the toluene contained a small amount of cobalt powder derived from the decomposition of carbonyl.

The OXO reaction was found to take place with a wide variety of pure compounds and technical materials containing ethylenic double bonds. It is clear that almost limitless possibilities are available for further processing of the aldehydes first formed, either by aldol condensation or conversion to the corresponding acids, in addition to conversion to alcohols, as in the "parent" process described above.

b. Production of High-Grade Lubricating Oil

Research work carried out by Ruhrchemie was successful in improving the oxidation stability of their synthetic lubricating oil. It was found that if 0·2–0·5% phenthiazine was added to the olefin stock used in the polymerisation, the viscosity increase occurring on oxidation of the resulting oil was only 20% compared with 150% for the oil prepared in the normal manner. A similar result could be obtained by incorporating ca. 0·3% elemental sulphur in the feedstock, although in this case it was necessary to subject the oil to a further treatment with 1% $AlCl_3$ at 250°C to reduce the sulphur content of the oil and remove objectionable odour.

It was proposed to use phenthiazine incorporation in a projected scheme for the production of 9,500te/yr of aviation bright stock of viscosity 50°E at 50°C and viscosity index ca.110. The raw material for this project was to come partly from cracking of saturated hydrocarbons recovered from the OXO plant, sweat oil from wax refining and middle oil purchased from other Fischer-Tropsch plants (total olefinic material 10,025te/yr C_9-C_{18}) and partly from the recycle "olefin synthesis" (7,440te/yr C_9-C_{10}). The recycle spirit was to be deoxygenated by passage over activated alumina at 340–350°C.

The polymerisation would be carried out using 4–6% of $AlCl_3$ at 15°C for 12hr, followed by 2hr at 60°C with the addition of phenthiazine. The finishing processes were to be the same as those used for motor oil.

The phenthiazine used was the crude product obtained by melting 1 mole diphenylamine with 2 moles sulphur in the presence of 2% $AlCl_3$, stirring for 8hr at 80–150°C and decomposing the melt with water.

c. Production of Toluene

Ruhrchemie had worked out the details for the production of toluene by the catalytic cyclisation of the heptane-heptene cut of Fischer-Tropsch primary products, and the construction of a plant to produce 24,000te/yr had been commenced, but was abandoned on Government orders when only 20% complete. The process was as follows:—

The C_7 fraction containing 15–20% olefins, was vaporised and preheated to 400°C, and passed at a rate of 0·15–0·20m³/hr liquid feed per m³ catalyst through a bed of Al_2O_3-Cr_2O_3 catalyst (containing 20% Cr_2O_3), maintained at 480–530°C by the heat set free in burning off the deposited carbon with air during the preceding regeneration stage. The time cycle was:—

Cyclisation	.. ..	30min
Purging with flue gas	.. .. ..	3 ,,
Regeneration with air	.. .. ..	15 ,,
Reduction in hydrogen	.. .. ..	5 ,,
Switching	.. ..	4 ,,

In pilot plant tests, a 90–92% recovery of liquid products containing 50% by weight of toluene was obtained, and carbon formation amounted to 1·5–1·8% of the feed. The catalyst life was given as two years, but during this period the working temperature had to be raised by 30°C, the yield of recovered product fell to about 85% and the proportion of toluene to 44%.

The total liquid product was fractionated in a column equivalent to 45 theoretical plates, the toluene fraction, containing 3–5% olefins; acid-washed and re-run to give nitration-grade toluene. The estimated cost of production of toluene in the projected full-scale plant was RM382/te based on a raw material (C_7 fraction) cost of RM300/te.

d. Production of Aviation Fuel

Ruhrchemie considered that the most suitable process for obtaining substantial quantities of aviation petrol from the primary products of the Fischer-Tropsch process was catalytic cracking to produce C_3, C_4 and C_5 olefins and conversion of these to polymer petrol.

They had developed a process in which the 170–350°C fraction of the primary product was cracked in the vapour phase at atmospheric pressure and 500°C in the presence of "Granosil" (an acid-treated clay). The conditions were arranged so that the heat required for the cracking reaction was obtained by burning-off the carbon deposited on the catalyst (as in the case of the toluene process described above). The period occupied by the burning-off process was about one-half that occupied by cracking. The C_3, C_4 and C_5 fractions (90% olefins) were separated, polymerised and the polymerisates hydrogenated, the fraction 60–165°C of the hydrogenated product being separated as aviation fuel. A blend of the C_4 and C_5 polymer spirits gave aviation fuel No. 1, octane number (Motor) = 90 (without lead). If the C_3 polymer was included, aviation fuel No. 2, Motor octane number = ca.85, was obtained. In the pilot-plant trials of this process a catalyst life of about five months was obtained and the yields of final products were as follows:—

		Aviation Fuel No. 1	Aviation Fuel No. 2
Aviation fuel %	..	31·7	56·1
Motor fuel % ..	..	48·1	23·7
		(ON = 87Res)	(ON = 80Res)
Liquified gas %..	..	8·8	8·8
C_2 (60% ethylene) %	..	6·2	6·2
$CH_4 + H_2$ % ..	..	1·6	1·6
Carbon %	..	3·6	3·6

A plant designed to treat 26–27,000te/yr cracking stock by this process was 60% complete when work was abandoned in 1944. The estimated cost of production, based on a charge of RM300/te for the cracking stock, was RM510/te aviation fuel.

e. The Oxidation of Fischer-Tropsch Hard Wax

The oxidation of wax was studied at Holten by Ruhrchemie with the object of producing emulsifiers and substitutes for Montan wax, which was in short supply. In order to produce the desired high molecular-weight acids, most of the work had been carried out with hard wax, mp ca.90°C. The most successful process developed involved oxidation with nitrosyl sulphuric acid obtained by saturating sulphuric acid with oxides of nitrogen obtained from Ruhrchemie's synthetic nitric acid plant. The process was as follows.

A batch of 100kg hard wax was stirred with 20kg of nitrosyl sulphuric acid at 120–125°C and gases from ammonia oxidation containing 8% NO_2 passed through at 65m³/hr. After 10–12hr the reaction was stopped, the acid layer removed and the upper layer washed with boiling water. The dried crude product which contained about 50% of unoxidised wax was known as "OP3." Its properties were:—

Acid no. ..	..	..	..	..	70–75
Saponification no.		..	..	..	80–85
Solidification point		..	..	..	80°C
Clear mp ..	..	..	..	..	90°C

To recover pure acids, this product was treated in a kneading machine with a 50% excess of 30% NaOH at 100°C until all the water had evaporated. The cooled mass was disintegrated and extracted with 80–100°C synthetic spirit and the acids recovered by treating the residue with sulphuric acid. This product, known as "OP32," had the following properties:—

Acid no. ..	..	..	..	..	145–150
Saponification no.		..	● ..	..	150–155
Solidification point		..	..	..	80°C
Clear mp ..	..	..	..	..	90–100°C

The wax recovered from the saponification could be returned for oxidation and in this way an 80% yield of OP32 could be obtained (based on wax converted).

The product was found to be suitable for preparing impregnants for the textile industry (water-resisting fabrics) and in the production of printing colours. By partial saponification very effective emulsifiers were produced for use in the preparation of shoe and floor creams, emulsion lubricants and drilling lubricants. Some of these products could be produced direct from the crude OP3. By bleaching OP32 with chromic acid-sulphuric acid mixture, a stable white product suitable for use in the preparation of skin-cream types of emulsion was obtained. The experimental plant produced about 3te/month of the crude product, OP3.

E—Crude Oil Production

1. INTRODUCTION

Although German oil supplies during the war were obtained from a number of sources, this report deals mainly with crude oil production obtained within the frontiers of Germany as it was before the invasion of Austria. Apart from a very small production obtained in the Upper Rhine Valley near Bruchsal, the whole of this production was obtained in the present British Zone (see Fig. 55). For various reasons it has not yet been possible to obtain an appreciation of the work done on petroleum production during the war throughout the "Greater Reich."

When the oilfields were overrun by the Allied Armies, it was found that the German technical men had made little effort to destroy the technical records, and the first task of the investigating party was to ensure that no essential data was lost; as a result it has been a relatively simple matter to compile an accurate account of the industry's activities during the war years. This report, however, does not confine itself strictly to war years as, for a proper understanding of the war developments in German crude oil production, it is necessary to review the preparations from 1934 onwards (Table LXV).

Table LXVI gives the 1944 monthly production figures sub-divided into finished products and well illustrates the high yield of lubricants amounting to nearly 50% of the crude oil production.

The following table extracted from captured documents, shows the monthly production in te during 1944.