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TECHNICAL REPORT No. 248-45

THE SYNTHESIS OF HYDROCARBONS AND CHEMICALS FROM CO AND H_2

Riehl, E. H.

September 1945

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TECHNICAL REPORT No. 248-45

THE SYNTHESIS OF HYDROCARBONS AND CHEMICALS FROM CO AND H_2

SUMMARY

It is the object of this report to describe the commercial application of and the development in Germany, in the Synthesis of Hydrocarbons and chemicals from CO and H_2 during the war.

September 1945

U. S. NAVAL TECHNICAL MISSION IN EUROPE

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SECTION VII (Cont'd.)

THE SYNTHESIS OF HYDROCARBONS AND CHEMICALS FROM CO AND H_2
THE FISCHER-TROPSCH PROCESS

Introduction

The synthesis of hydrocarbons from mixtures of CO and H_2, commonly referred to as the Fischer-Tropsch process, was the object of a coprehensive study by the U.S, Naval Technical Mission in Europe's Petroleum Group in Germany from April through June 1945.

This study disclosed that the process was of secondary importance in the German fuel economy, producing 9.1% of the total German oil supply. The concerted effort of German scientists to improve its two main drawbacks; very low space velocity and poor quality gasoline did not succeed which made it a poor competitor with such processes as coal tar or even coal hydrogenation. It was quite generally agreed in Germany that CO+H_2 Syntheses would be used in the future as methods of producing special chemicals and chemical raw materials.

The outstanding quick ignition, ash and sulphur free quality of the diesel oil from FT synthesis would not, in the German point of view, change this picture. No attempts were made to develop engines which could make use of the 90-100 cetane number in a pure FT diesel oil as such. The Germans, being short on all types of hydrocarbons, made good use of the "Cetane" from their FT plants, however, by upgrading diesel fractions from coal tars with cetane numbers of 10-15 and thus increasing their production of 40-50 cetane diesel oil. For this purpose, FT oil was exceptionally suited. The value of cetane number is presently undergoing a re-examination and until this re-examination has been completed, the further use of the Fischer diesel oil is uncertain.

The production of chemicals via synthesis from CO+H_2 was still in its early beginnings. The war has slowed down all research not directly connected with the German war effort; but two classes of compounds produced by Fischer-Tropsch synthesis, nevertheless, received particular attention; mono-olefines and high boiling alcohols. These compounds were of great interest, the first for polymerization to synthetic lube oil and for sulfonation to detergents; the second for esterification to special lubricants. The German efforts to increase and control production of these compounds were successful, in that they developed means to enrich these compounds in the primary synthesis products to concentrations of almost 70%.

Introduction (Cont'd.)

The ways used to obtain these yields are described in Sections 1a and 1b.

The FT synthesis is known to be but the sum-total of a great many different reactions, such as carbide formation, polymerization, hydrogenation, cracking, and isomerization. The direction of future research must necessarily be towards better insight into the chemistry of synthesis and the kinetics of the reaction. The Germans have done considerable work along this line and the information obtained from them is reported in Section 1b.

Finally, it is pointed out that only the actual synthesis is considered in this report. Methods to produce the feed ("$CO+H_2$"), as well as processes based on the primary products are described in the following U.S. NavTecMisEu reports:

(a) The production of H_2 and synthesis gas from Solid and Gaseous Fuels.
(b) The Manufacture and Application of Lubricants in Germany.
(c) The Manufacture of Aviation Gasoline in Germany.
(d) German Diesel Fuels.

SECTION I

THE FISCHER-TROPSCH PROCESS

Contents.

Present Commercial Application.

Contents (Cont'd.)

SECTION I.(a)

THE FISCHER-TROPSCH PROCESS

Present Commercial Application.

1. General Status of Process.

The Fischer-Tropsch Synthesis had reached commercial realization long before the war. It had attracted considerable interest in the United States and finally patent rights were obtained by certain American companies. Late in 1938 a thorough exchange of information took place in Germany followed by an inspection of the plants. Thus all information available at that time may be considered in American hands.

The greatest obstacle to a large scale development of the process was the poor quality of the gasoline it produced. With the beginning of the war only a short distance away, the Germans had to use other means to synthesize high quality fuels, such as high pressure hydrogenation, and in

1. General Status of Process (Cont'd.)

the same measure as hydrogenation capacity was increased, the expansion of Fischer-Tropsch was brought to a standstill. Thus we find, practically all Fischer-Tropsch plants completed and in operation before the war.

The main sponsor of the process, Ruhrchemie A.G. expended great effort to develop processes to improve the fuel quality of the primary product, but the fact was finally recognized that Fischer-Tropsch using cobalt catalyst primarily could be of value as the means to produce chemicals rather than fuels, with diesel oil a possible exception.

The first objective was the production of olefines and the subsequent conversion of the olefines to such products as synthetic lube oils or high-boiling alcohols. The Germans succeeded in this development.

The next step would be the direct synthesis of more valuable compounds, such as high-boiling alcohols and esters. The work done in this connection is described in Section 2 of this report (Synol).

In the following chapter, information is presented regarding operation, production and cost of product from existing plants.

2. Location and Production of Commercial F-T Plants in Germany.

During the war, Germany suffered from a great shortage of hydrocarbons, and the oil produced via FT represented a substantial part of the total domestic production as can be seen from the following table:

Source of Product	Total Capacity Tons/Year	%
H.P. Hydrogen'n	3,918,000	60.1
FT Synthesis	591,000	9.1
German Crude	1,920,000	29.5
Bituminous Coal Tar	36,000	0.5
Brown Coal Tar	50,000	0.8
@	6,515,000	100.0

@ Data from Dr. Buetefisch, Secretary Oil Section German Industry.

These figures give the installed capacity of the plants. It must be understood that Allied bombing substantially reduced production during the last years.

2. Location and Production of Commercial FT Plants in Germany (Cont'd.)

The first firm to operate FT plants was Ruhrchemie A.G. who sponsored the development of the process and exercised some control over all other plants through license and catalyst preparation and regeneration. There were only three plants in Germany where catalyst was made, 2 of which were under direct Ruhrchemie control. In the next table is given a list of the F-T plants which operated in Germany (a small unit is operated by the Kuhlmann Co. at Harnes, France, 11,000 T/year).

GERMAN FISCHER-TROPSCH PLANTS

Name of Operator	Location	Capacity		M tons/month - Avg.Monthly Prod			
		Tons/Yr.	%	Motor Gasoline	Diesel Fuel	Wax & Kogasin	Lube Oil
Ruhrchemie	Holten,Ruhr	72,000	12.0	2.1	0.8	1.4	1.2
Gewerkschaft "Viktor"	Castrop-Rauxel,Ruhr	40,000	6.8	1.5	1.0	0.8	-
Rheinpreussen L.u. GH.	Moers,Ruhr	70,000	11.8	2.8	2.1	1.1	0.2
Krupp Benzin	Wanne-Eickel, Ruhr	60,000	10.2	2.2	1.1	1.7	-
Hoesch Benzin	Dortmund, Ruhr	47,000	7.9	0.5	1.2	2.0	0.2
Braun Hohle Benzin A.G.	Ruhland, Saxony	170,000	29.2	8.4	2.5	3.1	-
Essener Benzin A.G.	Berghamen, Ruhr	80,000	13.6	4.1	1.8	0.8	-
Schaffpotsch Benzin Gm GH.	Deschowitz, Silesia	40,000	6.8	0.7	0.8	1.8	-
Wintershall A.G.	Luetzkendorf, Saxony	(70,000) 12,000	1.7	0.2	0.1	0.7	-
T O T A L :		591,000	100.0	22.5 (46.1%)	11.4 (23.3%)	13.4 (27.4%)	1.6 (3.2%)

2. Location and Production of Commercial FT Plants in Germany (Cont'd.)

Of the existing 9 FT plants, 5 were of the low pressure ("Niederdruck") type, 2 included both low pressure and medium pressure, and 2 were of the medium pressure ("Mitteldruck") type. The distribution of these plants and their capacities is shown in this table.

DISTRIBUTION OF LP(1) AND MP(2) CAPACITY AMONG FISCHER-TROPSCH UNITS
(Based on actual production for 1942)

Name of Plant	LP Operation T/Year	MP Operation T/Year	Total T/Year
Ruhrchemie	18,088	44,545	62,633
Viktor	37,699		37,699
Rheinpreussen	67,212		67,212
Krupp *	48,330	11,857	60,187
Hoesch		46,044	46,044
Brabag	164,606		164,605
Essener	79,974		79,974
Schaffgotsch		26,374	26,374
Wintershall	11,468		11,468
T O T A L :	427,377	128,820	556,197
%	76.8%	23.2%	100.00%

* In this plant the first stage operates at low pressure; second stage at medium pressure.

The last FT unit, a medium pressure plant, had been built in 1937 (completed 1939). However, it was found that this product was even less suitable for motor fuel due to its lower olefine content and no further units were built.

2. Location and Production of Commercial FT Plants in Germany (Cont'd.)

In the meantime, a new type of operation was developed, consisting mainly of gas recirculation ("Kreislauf") which, on MP operation gave substantial increase in the production of olefines. This process is described in detail in this report. Two of the existing MP plants were in the process of conversion to "Kreislauf" but neither had begun to operate and all information is based on pilot plant data. (1) Low Pressure; (2) Medium Press.

To give a more detailed picture of the production and product distribution of the FT plants, the following table has been prepared. This table is based on actual production for the year 1941. (the data was taken from the licensing invoices of RCH(1) to the 9 licenses).

Note that these figures do not agree with those shown on Table II which covers the following year. The difference is due to the addition in plant capacity in that period. By 1943 the decline in production caused by Allied air activity had already begun.

The figure, barrels/day, is only an approximation based on an average density of 7.5 lbs/gal. (See reference 1a at end of this section).

PRODUCT DISTRIBUTION OF FT UNITS FIGURES IN TONS/YEAR (1941)

Name of Plant	Fluessigas (gasol)	Gasoline	Kogasin (230-320°C)	Diesel Oil	Paraffin (Gatsch)	Hard Wax	Other Products not sold directly	TOTAL
Ruhrchemie	8988	20616		8454			14855	52913
Viktor	4471	18167	3358	7395	2927	833	24	37175
Rheinpreussen	7379	34191	6656	16394	5093	1408		71122
Krupp	4657	25531		11467	5575	2500	8645	58375
Hoesch	3591	9523	3749	15287	5788	351	6110	44055
Brabag	8421	77955		31845	9812	3230	8864	140177
Essener	10415	32574	4767	17007	6199	1351		72312
Schaffgotsch	1557	6035	56	5320	4441	1441	1640	20490
Winterschall	5	3388	838	631	503	195		5561
T O T A L :	49484	227980	19424	113800	40388	11309	40138	502175
%	9.81	45.57	3.86	22.50	8.00	2.55	8.00	100.00
Barrels/Day	948	4380	372	2175	755	216	770	9620

(1) Ruhrchemie Holten

2. Location and Production of Commercial FT Plants in Germany (Cont'd.)

Although German price figures are not a good basis for calculation in other countries, they were used as the basis for calculating license fees to RCH. The prices for different FT products are given below:

Fluessiggas: $C_3 - C_4$	22 - 26.6	Pfennig/Kg.
Gasoline: Stabilized	25.7-31.5	"
Diesel oil	23.0-27.0	"
Paraffin Gatsch	20.5-25.0	"
* Special Waxes	56.0-92.0	"

* This figure depending on melting point.

The total realization for the primary products for 1941 broken down according to plants was as follows:

Ruhrchemie	13,504,550 - RM/year	25.40	Rpfg/Kg.
Viktor	9,788,611 "	26.30	"
Rheinpreussen	20,467,303 "	28.70	"
Krupp	16,987,486 "	19.20	"
Hoesch	12,114,410 "	27.99	"
Brabag	42,141,536 "	30.20	"
Essener	20,677,082 "	28.50	"
Schaffgotsch	5,978,738 "	29.15	"
Wintershall	1,685,762 "	30.31	"
TOTAL:	143,345,478 - RM/year	28.4	Rpfg/Kg.

The license fee to Ruhrchemie A.G. was exactly 1% of the net sales value of the products.

For the year 1941:

Total Production:	502,175 ton/year
Total License Fee	1,433,454 RM/year
License	2.85 RM/ton product.

3. Catalyst.

(1) Supply of Cobalt Catalyst. (See reference I (a)/2 and I (a)/3 at end of this Section).

All existing plants (LP and MP) were operated with the Standard Ruhrchemie Cobalt-Thoria-Magnesia-Kieselguhr catalyst. This catalyst was supplied from 3 catalyst manufacturing plants.

3. Catalyst (1) (Cont'd.)

From the above tables it can be seen that the FT capacity in Germany was located in 3 different regions as follows:—

Location	Total Capacity (ton/year)	%
Ruhr	353,749	63.67
Saxony	176,074	31.60
Silesia	26,374	4.73
TOTAL	556,197	100.00

The three catalyst plants were located accordingly:

Name of Company	Location	Capacity (oven fillings/month) *	
Ruhrchemie	Holten	100	50.0
Brabag	Ruhrland	65	32.5
Wintershall	Luetzkendorf	35 **	17.5
TOTAL:		200	100.00%

* One oven filling : 10 M^3 : 0.9 ton cobalt (average)
** Later increased to 85 to make up for bomb damage at Holten.

The overall yearly German cobalt consumption for FT plants was between 85 and 95 tons. The cobalt resources of Germany were barely enough to keep all FT plants operating during the war, particularly with Finland the only supplier of the metal. There was no shortage of Thoria.

In the handling of the catalyst in the synthesis, and during reworking in the catalyst plants losses were incurred. These losses differed substantially between Ruhrchemie and Brabag. This may be due to the size of the plant and the fact that Brabag is a more modern installation.

The figures obtained in actual operation are as follows:

Plant	Loss of cobalt in Synthesis	Loss of Re-working	Total Loss
Ruhrchemie	4.0%	4.0%	8.0%
Brabag	1.0%	1.5%	2.5%

Based on a production of 400 tons primary product per ton cobalt catalyst and using the Brabag figure this would give 16,000 tons of product ultimately produced per ton of cobalt metal.

The production method of the catalyst has not been changed since 1938

3. Catalyst (1) (Cont'd.)

with the exception of a new forming and drying device which is described below.

The impending shortage of cobalt had led to a large scale development program to replace this metal with iron. This work was a continuation of earlier attempts to produce a better fuel over iron catalysts.

Research along this line was carried out by the following companies:

- I.G. Farben (along 4 or 5 different lines)
- Ruhrchemie
- Rheinpreussen
- Brabag
- Lurgi
- Kaiser Wilhelm Institut (Muehlheim)

The detailed result of these efforts is described in Section I.(b). While good catalysts had been developed for a variety of purposes, none was found that could replace cobalt in the existing units.

The operating temperature of iron catalyst is inherently above that of cobalt. Since the reactor cooling systems had been designed for steam pressures corresponding to cobalt operating temperatures, the substitution could not be successfully accomplished despite the claims of some companies.

4. Preparation of Cobalt Catalyst.

The Cobalt Catalyst used today differs only slightly from the one used in 1938 prior to the exchange of information between U.S. and German engineers.

Composition:		
	Cobalt (Co)	100 pts.
	Magnesia (MgO)	10 pts.
	Thoria (ThO_2)	5 pts.
	Kieselguhr	200 pts.

The same catalyst would also be used in the Kreislauf operation except for a higher Kieselguhr content (dilution).

The preparation of this catalyst up to the forming and drying of the filter cake was identical as in 1938. A new drier had been developed which would at the same time form the catalyst and give a minimum of abrasion loss in handling. The drier consisted of a drum of 2 m. long and 1.5 m. dia.

4. Preparation of Cobalt Catalyst (Cont'd).

The outside was studded with small toothed rails, which would serve as molds. The filter cake was pressed on to the drum and the indentation of the mold filled to give small (3 mm.) cylinders. The drum rotated slowly (0.1 RPM). At the same time hot gases were passed through the cake filled molds drying the catalyst particles before they would reach the bottom position of the drum, where having contracted slightly during drying, they drop out by gravity. Air or superheated steam could be used for drying purposes.

This method of handling the catalyst made it possible to use a Kieselguhr which had been processed at 700°C. and was softer than the material treated at 1000°C. The softer Kieselguhr gave a more active catalyst (apparent density 130-150 gm/100 cc.)

The reduction of the catalyst is carried out with dry CO_2 free gas ($H_2 - N_2$ mixture or H_2 alone). CH_4 is not a detrimental component of the reducing gas. H_2O, CO_2 CO, NO_2 are all undesirable. The presence of CO_2 is detrimental due to the shift-reaction, which is catalyzed, forming small quantities of CO. This CO is further reduced to CH_4 causing local overheating on the new and highly active catalyst.

The effect of CO_2 in the reducing gas is quite pronounced: with 1 gm/m^3 gas, the reduction is 50%. With no CO_2 in the gas, reduction is 60-65%.

While reducing the catalyst, the necessary heat is supplied with the reducing gas. A temperature of 400°C is reached within 3/4 hours and maintained for a very short time to complete the reduction. The CoO; CO; H_2O; H_2 equilibrium at 400°C governs the extent to which the oxide is reduced. Co. 60%- CoO 40% is the correct ratio in a good catalyst. The extent of reduction is determined by measuring the $cm^3 H_2$ evolved from a known weight of catalyst, upon addition of H_2SO_4.

For the production of olefines both RCH and Lurgi proposed to thin out the catalyst with more Kieselguhr, the catalyst otherwise being identical. About 250-300 pts. Kieselguhr would be used instead of 200 pts. for every 100 pts. of cobalt.

5. Production Data from Commercial Large Scale Operation.

(See reference I (a)/5 and I (a)/6 at the end of this Section).

In the following paragraph some commercial operating data from the largest FT plant are given. Since most processing details are known in the

5. Production Data from Commercial Large Scale Operation (Cont'd.)

United States, it was considered more important to report the overall results rather than describe minor operational changes during the war, which revolve around variations of space-velocity, or catalyst life and similar problems.

No basic changes were made in the actual operation of FT plants up to the collapse of Germany. The data posted below were taken from the balance sheet of the Brabag Plant at Ruhland, covering operations in 1943 and 1944. The plant in question is the largest FT unit. It is of the two-stage LP type using standard cobalt catalyst.

For the year 1943 the following figures are given; they are monthly averages based on the entire 12-month period of Jan. 1 to Dec. 31, 1943.

(1) Gas Production.

Total Synthesis gas produced	116,736,300 m^3/month.
$CO+2H_2$ in gas	79%
Yield of gas from brown coal briquets	1.107 m^3/ton

(2) Synthesis.

(a) Production:

Kondensatoel	6306.1 ton/month	52%
Primary Gasoline	5842.0 " "	48%
Liquid products total	12,148.1 ton/month	100%
Pure gasol	2,836.7 " "	23.2%
Total	14,989 ton/month	
Tailgas	42,165,100 m^3/month	
	- 30.1% of gas feed.	

(b) Yields:

Liquid products/ton briquet	127.4 Kg.
Pure Gasol/ " "	29.8 Kg.
Total:	157.2 Kg.
Liquid products/m^3 Gas	104.1 gram
Pure Gasol " / "	24.3 gram
Total:	128.4 gram

(3) Processing of Primary Products.

(a) Production of materials for sale.

Gasoline	6532.3 tons/month
Gasoline in diesel oil	569.7
Diesel oil	1987.6

5. Production Data from Commercial Large Scale Operation(3)(Cont'd.)

(a) Production of materials for sale(Cont'd.)

Adsorber gasoline bottoms	557.5	tons/month
Adsorber gasoline	703.1	"
Paraffingatsch	1160.5	"
Kogasin II	2085.1	"
Liquified gases	1228.4	"
Wax	454.4	"
TOTAL	15178.6	tons/month
From outside sources	415.8	tons/month
From Synthesis proper	14762.8	"

(b) Yields:

Sales products/tons briquets	154.6	Kg.
Sales products/m^3 Synthesis gas	126.5	gram
Sales products/ton Primary Product	982.0	Kg.

(4) Financial Statement.

(a) Balance:

Out of pocket Cost	3,005,000	RM/month	199.21	RM/tons
Overhead and license	187,000	"	12.40	"
* Capital interest	688,000	"	45.61	"
Amortization	1,118,000	"	74.12	"
TOTAL:	4,998,000	RM/month	331.34	RM/tons
Sales:	4,739,000	RM/month	314.17	RM/tons
Loss:	259,000	RM/month	17.17	RM/tons

* Note the capital cost is excessive. This may have been for reasons not connected with operation of the plant.

(b) Cost Breakdown.

(1) Material Cost	RM/month	RM/ton prod.
Briquets (at RM 9.60/ton)	920,000	60.99
Outside Coke(at RM 34./ton)	304,000	20.15
Grude Coke (at RM 23./ton)	66,000	4.38
Raw coal (boilers)(at RM 2.4/ton)	14,000	.92
Outside power (at Rpfg. 1.9/KWH)	61,000	4.04
Catalysts	145,000	9.61
Purification (charcoal)	18,000	1.20
Licenses	47,000	3.12
TOTAL:	1,575,000	104.41

5. Production Data from Commercial Large Scale Operation (4)(Cont'd.)

		RM/month	RM/ton prod.
(1)	Material Cost		
	Income from $NaNO_3$ (RM 95./ton) and other chemicals (RM 35./ton)	154,000	10.21
	Net Total Materials Cost	1,421,000	94.20
(2)	Other Costs.		
	Hourly Wages	706,000	46.80
	Salaries	290,000	19.23
	Other costs	635,000	42.10
	Overhead	140,000	9.28
	5% capital interest (basis: 165 million RM)	688,000	45.61
	9% Amortization (basis: 149 million RM)	1,118,000	74.12
	Total Operating Expense:	4,998,000	331.34

It is interesting to compare the operating costs of HP Hydrogenation with FT synthesis. The Brabag, aside from operating the largest FT plant, also owned three (3) HP Hydrogenation units. Some comparative figures for those plants are given here. They are based on the second quarter of 1943.

	FT (Ruhland)	HP Hydrogenation (Boehlen)
Primary Product	15,201	21,630 tons/month
Total Production Cost	307.67	251.20 RM/ton prod.
Feedstocks		
Browncoal Tar	-	1.223 ton/ton prod.
Browncoal coke	-	0.803 ton/ton prod.
Browncoal briquets	5.791	- ton/ton prod.
Utilities		
Steam	11,635	3,346 ton/ton prod.
Water	218,219	247,600 m^3/ton prod.
Power	836	1,210 KWH/ton prod.
Investment (Interest and Amortization)	732.29	323.79 RM/ton prod.
Production	3.384	5.570 ton/month/employee

The comparison may not be fair on all accounts since these plants were operated under wartime conditions with Ruhland employing about three times as many foreign workers as Boehlen. This fact may be of importance.

6. Operating Conditions.

The main variables of the operation, such as pressure, temperature, space-velocity, gas composition are today practically the same, as in 1937-1938. Specifically, there was no improvement or change in the design of the ovens. Nevertheless there was no increase in the average yield expressed in gram/m^3 feed gas from approximately 100 g to 130 g/m^3. As Germany was faced with a serious lack of cobalt, the yield of product per ton of cobalt was of greatest importance, since this yield can be raised by keeping the space-velocity low, most plants were operated at less than 100 V/H/V (Vol feed gas/hr/unit volume catalyst).

The Essener Steinkohlen A.G. apparently had developed a somewhat improved method of operation, which resulted in a better yield based on feed, and longer catalyst life. This operation widely discussed by the FT group, was known as the "Essener Fahrweise".

In principle, it consisted only in a rigorous control of operation, i.e.;

(1) Absolute constant feedgas rate and composition.
(2) Countercurrent regeneration of all ovens.
(3) Low-space velocity (increased number of ovens).
(4) More equal distribution of load between stages.

With these means the Essener plant obtained the following results:

	Essener	Others
Yield	160	130 C_3+ gm/m^3 gas.
Catalyst life	2000	1400 hours
Catalyst yield	425	250 ton/ton catalyst

Flexibility of Operation. In order to show the variations possible in FT plant operation, yields and product qualities for 2 conditions listed below. The data are based on a report from Brabag and refer to their Ruhland plant:

	Case I	Case II
Processing		
Absorber gasoline	160°C EP	140°C EP
Diesel oil	160-300°C Max.	under 325°C
Gatsch	over 325°C	over 325°C

6. Operating Conditions (Cont'd.)

	Case I	Case II
Yield.		
Gasol	5100 ton/year	7600 ton/year
Gasoline	73800 "	83900 "
Diesel oil	52500 "	35100 "
Gatsch	10100 "	10100 "
	141,500 ton/year	136,700 ton/year
Products		
Gasoline: sp.gr.	0.686	0.689
Octane No.	56	62
Diesel oil: sp.gr.	0.757	0.732
Pourpoint	- 20°C	- 60°C
Flashpoint	+56°C	+25°C
Vis E/20	1.08	1.022
Cetane No.	100	88

The difference is due to a variation in the amount of thermal cracking of the distillation fraction carried out in a separate unit.

7. Medium Pressure Fischer-Tropsch Units.

(a) General. The medium pressure units were expected to give more higher boiling materials, particularly wax and also to have a longer catalyst life. However, they had the disadvantage of giving a very paraffinic gasoline (still the most important product) with a lower octane number.

In the meantime processes had been developed which used Fischer olefines as feedstock, and it became necessary to revise operations to produce a maximum of olefines. The Germans succeeded in these attempts. The development was carried through by Ruhrchemie, Hoesch, and Lurgi. By the end of 1944 the RCH and Hoesch plants had substantially completed the construction of equipment to produce a maximum of olefines on their MP-FT units.

The process used consisted in a combination of staging and gas recycle ("Kreislauf"), the operating temperature being substantially unchanged. Plants could still use the original reactors and the standard cobalt catalyst as furnished by Ruhrchemie.

(b) Development of 3-stage Operation. The Hoesch MP pilot plant had

7. Medium Pressure Fischer-Tropsch Units (b)(Cont'd.)

been designed to operate on the same 2:1 H_2: CO gas as the LP units, but it was soon found that the gas formation (CH_4) could be suppressed by lowering this ratio. The plant was operated on a feed ratio of 1.94:1 with the following results:

Average Values over Four Months.

Feed Gas:	81% CO+H_2	
	Conversion	90.8%
	Gas formation	23.1%
	Gasol " (C_3 C_4)	6.1%
	Liquid Product	126.2 g/m^3 ideal gas.
	Total Product (incl. C_3 C_4)	138.43
	Average space velocity	569 m^3/oven
	Average life of catalyst	4015 hrs.
	Coke requirement	4.99 kg/kg recovered product.
Primary Liquid:	Gasoline - 200°C	48.3%
	Kogasin - 320°C	26.9%
	Hard wax - 450°C	8.9%
	Olefine content of C_3 C_4	15 %

Following one year of operation at this condition, the H_2/CO ratio was further decreased to 1.8:1. This resulted in improved liquid yields, higher olefine content and lower gas formation. Unfortunately the average catalyst life decreased from 4015 hrs. to 2306 hrs.

In view of this improvement it was decided to further lower the H_2/CO ratio to 1.6:1. Since the ratio of consumption averages nearly 2.15:1, hydrogen had to be added to convert the remaining CO in the second stage. The ratio in the exit gas from the first stage was only 1.04:1. Hoesch had to use converted watergas with a ratio of 3.79:1 to correct the ratio as no hydrogen was available.

With the low ratio of H_2/CO_2 fed to both stages, the total conversion was found to be low. It was therefore decided to add a third stage preceded by another addition of hydrogen (converted watergas) to the exit gas from the second stage. Since this gas is quite high in inert content, the V/H/V and temperature in this final clean-up stage are rather high and correspondingly fewer ovens (10-17% of the total) are required. Results from three-stage operation are as follows:

7. Medium Pressure Fischer-Tropsch Units (b) (Cont'd.)

Average Values for Five Months.

Conversion	95%
Gas formation	18.1%
Gasol formation	6.7%
Liquid product	144.4 g/m^3 ideal gas
Total product (incl. C_3+C_4)	156.6 "
Average space velocity	607 m^3/oven
Average catalyst life	2745 hours.
Coke requirement	4.35 kg/kg recovered product

Primary Liquid

Gasoline	42.8%
Kogasin	25.8%
Hard Wax 450°C	14.6%
Olefine content of C_{3+4}	35 %

In order to show the conversion, the gas analysis in the three stages are listed:

	Feed 1st stage	Exit 1st stage	Feed 2nd stage	Exit 2nd stage	Feed 3rd stage	Exit 3rd stage	Convert gas	Total Plant
CO_2	8.6	20.2	16.3	30.8	27.3	37.9	5.0	7.9
Cn.Hm.	-	1.1	0.9	1.6	1.3	2.0	-	-
CO	33.0	29.7	27.1	20.7	20.5	14.5	18.8	30.8
H_2	53.5	30.6	40.5	15.7	22.8	6.5	70.6	56.3
CH_4	0.4	7.4	5.7	13.6	12.3	17.4	0.4	0.4
N_2	4.5	11.0	9.5	17.6	15.8	21.7	5.2	4.6
Ideal	86.5	-	67.6	-	43.3	-	89.4	87.1
H_2/CO	1.62	1.04	1.49	0.76	1.11	0.45	3.76	1.83

Note: The low H_2/CO ratios; they cannot be used in LP units.

The favorable results of this operation with low H_2/CO ratio to increase liquid yield led to the adoption of the three-stage operation in all three MP units.

8. Kreislauf Operation.

(See also reference I(a)/10 and I(a)/11 at end of this Section).

8. Kreislauf Operation (Cont'd.)

While the specific output had thus considerably been improved, there was still the low olefine content of the products which had to be overcome. This was finally done by the use of gas recirculation.

It had been found that at higher pressure the cobalt catalyst reduced the CO almost exclusively under formation of H_2O. Thus it is possible to feed a mixture to the reactor, with very high CO: H_2 ratio, without at the same time losing any CO to CO_2. The increase in the ratio does however raise the olefine content of the product. The tailgas of such an oven is obviously very high in CO and low in H_2 and thus affords a means to further increase the CO/H_2 ratio of the feed to this oven by recycling the gas, preferably after removing all products. This is important to prohibit possible hydrogenation.

The operation with Kreislauf is thus simply an extension of the three-stage operation described above. In practice, it was found that any increase in the ratio recycle-gas: feed-gas over 3:1 does not give sufficient further increase in olefines to warrant the expense. The olefine content of the gasoline cut (200°C EP) is around 70%, the Kogasin cut (200°-325°C) is around 45%.

The temperature required to give adequate conversion is somewhat higher than in ordianry cobalt operation but does not exceed 225° C. This can be reached with the existing steam-cooled reactors.

The Kreislauf was considered of great importance and the entire MP section of the RCH plant was to be used as first stage with Kreislauf. The LP Section would be operated with the exit gas from the MP plus the required hydrogen addition to give the 2:1 ratio, which is imperative in LP cobalt plants. In this arrangement 80% of the total plant production would have come from the Kreislauf.

Pilot Plant Data on Kreislauf Operation. At Hoesch a single reactor had been operated at length with gas recirculation and data from two identical ovens, one with, the other without Kreislauf, are given below:

	Kreislauf	Once Through
Space velocity (basis 10m^3 cat.)	1060 m^3/hr	1015 m^3/hr.
Ideal gas "	861 "	827 "
Catalyst space velocity	1.35 m^3/hr/kg cobalt	1.23m^3/hr/kg cobalt
Contraction	69%	57%
CO Conversion	85%	69.5%

8. Kreislauf Operation (Pilot Plant Data on Kreislauf Operation)(Cont'd.)

	Kreislauf	Once Through
$CO+H_2$ Conversion	89.8%	74.3%
Temperature	195° C	189° C
Average daily production(liquid)	2715 kg.	1835 kg.
Yield	131 gm/m^3 ideal gas	98 g/m^3 ideal gas

The test oven was operated 3650 hours. During the first 2764 hours (almost four months) the oven temperature remained unchanged at 195°C, the pressure at 7 atm. The space velocity was 1200 m^3/hr. for 1 month and 1000 m^3/hr. for the rest of the period. Recycle to fresh feed ratio was 2:1 in the beginning and later raised 3:1, but the difference in the result was not large within that range. The oven contained 2660 kg. catalyst with 785 kg. cobalt. The catalyst was the standard cobalt catalyst used throughout the plant.

The advantages derived from this operation are as follows:

(1) The oven may be brought on stream without loss of time usually required for this operation. In about 5 hours the oven is in full production. Synthesis gas is allowed to enter slowly and the recycle blower is started up while at the same time the pressure is allowed to build up. This is done at around 100° C. Next the temperatures is raised and fresh gas is added as the conversion starts in order to keep up the pressure. Finally the exit valve is opened and the unit is on stream.

(2) The yield per cubic meter synthesis gas is increased. Thus in the first stage alone, the same yield may be reached as formerly in two stages.

(3) Higher space velocity. Therefore fewer ovens are required for a given output. The increase is in the ratio of 3:2 if compared with two-stage once-through operation.

(4) Lower catalyst cost. This is apparent from (3).

(5) The unit is less susceptible to operating disturbances of variation in feed gas composition.

(6) Higher olefine concentration in the products.

In general the application of recycle lowers the boiling point of the product towards lighter materials, but this may be corrected by raising the $CO:H_2$ ratio as described above.

9. Cost of New FT Plants.

(See also reference I(a)/7 at end of this section).

It is interesting to note German figures on the cost of Fischer synthesis plants. The following data was obtained from Lurgi; (Basis 100,000 T/year plant)

Synthesis section and recovery 400 RM/ton year product.
This based on newest Fe catalyst using Kreislauf and Staging.
Complete Unit including Gas generator 900 RM/ton year product.
These costs are high compared with the following figures from I.G. based on Cobalt multiple stage operation without Kreislauf:

Synthesis section and recovery	290	RM/ton,	year	product
Complete unit including generator basis coke:	590	"	"	"
Complete unit including conversion basis natural gas:	500	"	"	"

The I.G. figures are based on 180,000 T/year capacity. When the plant size is reduced to 100,000 ton/year the cost of the complete unit (basis coke) is increased to 615 RM/ton, year product.

10. Products from Fischer-Tropsch Plants.

(See also reference I(a)/12 and I(a)/13 at end of this section).

During the last years the use of primary Fischer products was of course governed by wartime necessity. In general, it may be stated that a peaceful development would probably have led to the eventual disappearance of the FT product from the fuel picture, with the possible exception of the Diesel cut. Yet it was just this fraction that was also the starting material for a number of syntheses. As to the value of the diesel oil, it remains to be seen whether FT oil may have other special properties which are not yet recognized today, which make it highly desirable as a diesel fuel. The cetane number is, of course, known to be high (90-100). In Germany the fuels were used exclusively to blend up certain low cetane stocks like coal tar oil.

The properties of the LP and MP cobalt synthesis are well known and listed below:

(1) "Gasol-Fluessiggas" C_3 and C_4. The olefine content is fairly high as shown on the next page:

10. Products from Fischer-Tropsch Plants (1)(Cont'd.)

LP gasol contains 50-55% olefines
MP " " 25-30% "

Kreislauf would have produced 80% olefine in this fraction. The ratio of $C_3:C_4$ is approximately 1:1, with the butane cut containing 1-20% isobutane. This gas is used widely in Germany as a motor fuel and is bottled in the plants.

(2) FT Gasoline. In one case (Rheinpreussen) these olefines are used in the manufacture of isopropyl and isobutyl alcohols by sulphuric acid hydration. The bulk of the fraction is used as motor fuel. In many cases it is blended with benzene which is usually available from adjacent coking plants. No FT gasoline is used for aviation purposes.

The following properties are generally given:

	LP	MP
For 150°C EP gasolines:		
Olefine content	33%	19%
Octane No. (Res.)	57	38
For 200°C EP gasolines:		
Octane No. (Res.)	43	25

The product has a straight chain character. It was found that on the average one out of thirty carbon atoms was a tertiary.

Rhurchemie had developed processes to improve the quality of the gasoline. These include catalytic cracking, aromatization, olefine isomerization. These processes are dealt with in U.S. Naval Technical Mission, Eu. report entitled, "The Manufacture of Aviation Gasoline in Germany."

(3) Diesel oil. This fraction commonly called "Kogasin" ranging from 150 to 325°C was used either as fuel or raw material for chemical synthesis.

Diesel fuel was prepared by blending FT product with certain low cetane stocks (~~coal tar, hydrocoal tar~~, residueum) to give a 40-45 cetane diesel fuel. According to the season, a lower or higher pourpoint was required. This was obtained by cutting the fractions at various points.

	Summer	Winter
Diesel fuel	150°- 320° C	150°- 250° C
Cloud point	-6° C	-26° C
Pour point	-12° C	-34° C

The FT oil was blended in varying ratios with the tarоils according to the required cetane number.

10. Products from Fischer-Tropsch Plants (3)(Cont'd.)

A tar oil oil of 20 cetane, blended with 100 cetane kogasin, required the following percentage of kogasin:

For a 30 cetane blend	10%
For an 83 cetane blend	60%
The diesel fraction contains	10-15% olefines
MP operation gives a slightly better diesel fuel than LP operation	

The olefines boiling in the diesel or kogasin range are of great value as charging stock to certain syntheses. The preferred compound is the dolefine (terminal double bond). In general, the $C_9 - C_{11}$ olefines were used for polymerization to synthetic lube oil. The olefine content could be increased by a mild thermal cracking to 60-70% olefines. It was hoped, that the "Kreislauf" operation would produce this concentration in one step.

The $C_{11} - C_{17}$ olefines were used in the oxosynthesis. (See Section 7 of this report.) Here again it was hoped that the Kreislauf would produce fractions sufficiently rich in olefines to be fed directly to the synthesis without previous concentration.

(4) Wax. Waxes are the highest boiling product from FT operations It was for that reason that MP operations became of interest, since they yield somewhat more wax. The wax is obtained as bottom product in the distillation of primary products and by extraction of the catalyst (intermediate regeneration).

The waxes contain practically no olefines. Wax from MP operation has considerably less Isoparaffins compared with LP wax (less than 50% versus 40%). This is an important property, when the wax is to be used for oxidation to fatty acid, since the soaps derived from these acids were found to have superior odor. It is also of importance in the manufacture of lube oil by cracking and Al Cl_3 polymerization, straight chains being preferred. The wax is usually fractionated, with the lower melting part going to cracking (for lube oil synthesis) and the high melting point waxes (100°C) being sold as premium products.

Considerable work was done on the structure of FT waxes. An attempt was made to isolate pure compounds from the hard waxes by fractional crystallization in different solvents. The wax, a product obtained by extraction of spent catalyst from LP operation, was analyzed and the various fractions checked for melting point, molecular weight and other properties.

10. Products from Fischer-Tropsch Plants (4)(Cont'd.)

The following data were given:

Pour Point	Molecular Weight
63° C	400
84° C	600
96° C	800
106° C	1000

It was found that the synthesis produced all alipathic paraffins from C_1 up to C_{75}. The "Hard Wax" included the range from C_{25} to C_{75}. Indications were that some still longer chains were present. These higher fractions were hard brittle products which could not be scratched with a finger nail.

11. Adsorption of Hydrocarbons on Activated Carbon.

The art of adsorbing the heavier fractions from hydrocarbon gases on activated carbon with subsequent recovery of these fractions by steaming the carbon has been known and practiced for many years. The principal use made of this process by the Germans was the recovery of the so-called "Gasol" (C_3-C_4) fraction from the Fischer-Tropsch synthesis. Adsorption on carbon is peculiarly adapted to this purpose because a large proportion of the reaction product from the low pressure synthesis is not condensable at 20° C, but passes through the condenser with the residue gas. The process operates effectively at low pressure (atmospheric).

A diagram, (reference I(a)/15 at end of this section) showing the method of operating an activated carbon unit fro "Gasol" recovery is included in the appendix. In this scheme the feed gas is Fischer synthesis residue gas from which the gasoline and heavier components have been condensed by water cooling. In operation, at least four adsorbers are required. Each chamber is used successively for adsorption, drying and cooling.

The feed passes from bottom to top through adsorber one, which is in the adsorption stage. There the heavier components are adsorbed on the activated carbon. The lean stripped gas goes to the drying cycle, where it is picked up by blower 5, and heated from 100° to 150°C, in heater 6 along with some circulated dry gas. This gas then passes through adsorber 2, to dry the wet carbon bed which has just been steamed in the desorption stage. The hot wet gas from adsorber 2, is dewatered in cooler 7, and a large part of the dewatered gas is recycled through blower 5 as shown.

11. Adsorption of Hydrocarbons on Activated Carbon (Cont'd.)

The remainder, equivalent in volume to the gas from adsorber 1, goes to blower 8, and is further cooled in cooler 9. It then passes through the hot carbon bed of adsorber 3 to cool this bed preparatory to re-entering the adsorption stage. The gas leaving adsorber 3, is partially returned to the cooling cycle while the remainder leaves the system as lean residue gas to be used as fuel or for another synthesis stage.

The circulation is so controlled that when adsorber 1 has reached the limit of its adsorbing capacity, adsorber 2 is dry and adsorber 3 is cool. At this point the valves are automatically changed as follows: Adsorber 1 to desorption, 2 to cooling, 3 to adsorption, and 4 (which has been steamed out) to drying. The series flow of the gas through the three stages serves the additional purpose of picking up any heavy hydrocarbons, that carried through the first adsorber near the end of the adsorption period, in cooling the carbon bed of the third adsorber. This, of course, permits a greater loading of the carbon with the attendant economy of steam.

The desorption is performed with steam, and the gases are driven out of the carbon in the order: CH_4, CO_2, C_2H_6, C_3H_8, and heavier. The three-way valve 12 in the outlet line is open to the inlet of the adsorbing carbon chamber until the CO_2 and CH_4 are driven off in order to recover the small amount of heavy ends that come off. As soon as the C_3 and heavier gases begin to appear, valve 12 is switched so that mixture passes to condenser 13. Here the gasoline and water vapor are condenser by indirect cooling. This condensate is sent to separator 14 where gasol, gasoline, and water fractions are removed. The gasol goes to holder 15. The gasoline goes through after cooler 16 and meter 17 to tank 18. The water condensate is removed from the system.

The gasol from the holder goes through a compression and liquifaction cycle from which the uncondensable portion is recycled to adsorption and the liquid is sent to an intermediate storage tank. The pressure on this tank is maintained by bleeding gas back to holder 15. The gasol and gasoline are both pumped over a cooler and fed together to stabilizer column 19, where stabilized gasoline and merchantable gasol are removed, the rich overhead condensed gas is fed into the stream to the adsorber of the desorption step. At the beginning of the desorption, this gas, since it is quite rich, displaces CO_2 from the carbon bed during the first minutes of desorption, and therefore does not appear in the recycle to the adsorption vessel but goes to condenser 13, thus again saving steam for the

11. Adsorption of Hydrocarbons on Activated Carbon (Cont'd.)

process by higher loading of the carbon.

The carbon-adsorption is sometimes operated as a two stage process. The following operating data were given by the Lurgi Company.

	First Stage	Second Stage
Number of adsorbers	7	4
Diameter of adsorbers, m	5	5.5
Weight of carbon per adsorber, kg.	15,000	18,500
Inlet gas, m^3/hr.	35,000	21,000
C_3+inlet gas kg/hr.	3,400	1,500
Recovery		
C_5, %	100	100
C_4, %	60	100
C_3, %	10	80-85
Steam consumption, Kg/Kg.		
Recovered material	2.5-3.0	6.0-6.5
Time cycle, Adsorption, hrs.	1	1/2
Desorption, hrs.	1	1/2
Drying, hrs.	1	1/2
Cooling, hrs.	1	1/2

In the above cases, the carbon used was known as "Supersorbon". It was made from peat and activated by a Zn Cl_2 - steam treatment. The size of the carbon was 10%, 2.0-3.3 mm. and 90%, 3.3-4.0 mm. A carbon charge will remove about 1000 kg. of gasoline and gasol per kilogram of carbon before reactivation became necessary. It can be reactivated with steam at 800°C in a rotary kiln.

The Lurgi Company has developed a new carbon known as "SK" which is activated with K_2S, and is said to have about twice the capacity for low boiling hydrocarbons as "Supersorbon". The entire output of this carbon was used for gas masks during the war. Its absorption power for benzol from air as compared to that of the "Supersorbon" is presented below:

Concentration of Benzol grams/ m^3 air at 20° C	Adsorption in grams C_6H_6/100 g C	
	"Supersorbon"	"SK"
298	49	58
32	40	51
3.2	22	43
0.32	15	31

11. Adsorption of Hydrocarbons on Activated Carbon (Cont'd.)

A reprint of an article by Drs. Herbert and Ruepping entitled "Benzin und Gasolgewinnung mit Aktivkohle aus den Restgasen der Benzinsynthese nach Fischer-Tropsch, Ruhrchemie"; is included in the appendix of this report. This German article gives data on the recovery of hydrocarbon from Fischer-Tropsch residue gas, including the composition of the desorbed gases from minute to minute.

(See also reference I(a)/14 at end of this section).

SECTION I. (a)

12. List of References.

THE FISCHER-TROPSCH PROCESS PRESENT COMMERCIAL APPLICATION

The German documents listed below are available in the library of the Bureau of Ships at Washington, D.C.:

1. Iizenzabrechnung 1943 - 2 May 1944 Ruhrchemie A.G. letter incl. nine sets of licensing invoices.
2. "Iroerterung d. Kobaltlage", 8 January 1943.
3. "Kobaltkontakt fuer Fischer Anlagen", 19 April 1943, Note from Dr. Gloth to Dr. Altpetor.
4. "Fischer Synthesis Anlage Courrieres Kuhlmann", I.G. Report 3 December 1940.
5. "Betriebsergebnis April-Juni 1943" Operating sheet and Statement. Brabag (Schwarzheide, Boehlen, Magdeburg, Zeitz).
6. "Kosten Vorbericht - Schwarzheide" March 1944 - Brabag statement.
7. "Fischersynthese" 100,00 jato: cost estimate, 11 January 1944.
8. "Bericht (No. 317) uber die Kohlewasserstoffsynthese Versuche", Leuna, February 1939.
9. 1 Process flowchart: Krupp A.G. Wanne Eickel.
10. 1 Process flowchart: Lurgi "Kreislauf" Process.
11. 1 Flowchart for Hoesch "Kreislauf" plant, Lurgi drwg. ODS/592
12. Dipl Arbeit W. Beier (Rheinpreussen) 1938 "Erstarrungsverlauf von Paraffingemisch".
13. "Bestimmung des Isoparaffingehalts", I.G. Ludwigshafen by Dr. Leithe, May 1939.
14. "Benzin-und Gasolgewinnung mit Aktivkohle", by Herbert u. Rueping, Lurgi Company.
15. 1 Lurgi Drwg. OAK/121836 charcoal plant flowsheet.

SECTION I. (b)

GENERAL INTRODUCTION

Development Work - The Fischer-Tropsch Process.

The research carried out in Germany connected with FT operations was directed along the following lines:

Objective	Means Used to Reach Objectives	Name of Organizations Connected with Work
Replacement of Cobalt catalyst in existing plants	Development of Fe catalysts	KWI, Lurgi, RCH, Rheinpreussen, I.G., Brabag
Production of Olefines and wax	Fe catalysts in general	Same as above.
Production of alcohols	Fe catalysts ("Synol" Process)	I.G. (Leuna)
Improved design	Liquid phase Synthesis	Rheinpreussen, RCH, I.G.

This list does of course not claim to be all inclusive but gives the four subjects which appeared to be of greatest interest. It should be understood that item 1, is simply a wartime necessity. While Fe catalysts are generally considered superior to cobalt for a variety of reasons, they do not lend themselves for use in existing LP reactors. The work done on item 1, may be considered as supplementary to item 2.

(1) Fe Catalysts - General. Historically, Fe catalysts are older than cobalt. The first synthesis was carried out in 1922 over Fe catalysts. These tests were conducted at high pressures (100 atm.) and temperatures (400°C). The results were exclusively oxygenated compounds. With decreasing pressure the oxygenated fractions of the products decreased until at around 7 atm., the yield was almost exclusively hydrocarbons.

The decrease in pressure resulted in a corresponding drop in reaction velocity. It was therefore necessary to develop more active catalysts. At the temperatures employed at the time (400° C) these active catalysts

(1) Fe Catalysts - General (Cont'd.)

had a short life and for this and thermodynamic reasons the temperature had to be lowered further (from 400°C to 200°C) which in turn required still more active catalysts. Cobalt was found to fulfill the requirement and iron was temporarily shelved.

Nevertheless, work on iron catalyst was continued because the lower cost and higher production of olefines were were obvious advantages. The main difficulty was the low activity forcing the operation into a temperature range where CO decomposition (carbon deposit) may occur and where the lighter members of the paraffin homologues are more likely to be found. (This conversion at higher temperature under otherwise equal conditions yields more methan and gasol.)

Before going into some of the details of the German development of iron catalysts it seems appropriate to consider the effect which the elevation of the temperature range has on the equilibrium of the FT reaction. (See reference I(b)1 and 1(b)2 at end of this section). At first it can be shown that lighter products may be expected at higher temperature, other conditions being equal.

The following table gives values of the equilibrium constant "K" for the Fischer-Tropsch reaction for different temperatures and different members of the hydrocarbon series.

The values were calculated by P. Dolch, for the equation:

$$CO + \left(2 + \frac{1}{n}\right) H_2 \longrightarrow \frac{1}{n} \cdot C_nH_{2n+2} + H_2O$$

$$K = \frac{(C_nH_{2n+2})^{\frac{1}{n}} \; (H_2O)}{(CO) \quad (H_2)^{\left(2+\frac{1}{n}\right)}}$$

Compound	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_6H_{14}	C_8H_{18}
Temperature						
100° C	-17.69	-13.56	-12.17	-11.67	-10.77	-10.44
200° C	-11.32	- 7.93	- 6.85	- 5.53	- 5.35	- 5.49
300° C	- 7.15	- 4.27	- 3.38	- 3.18	- 2.50	- 2.26
400° C	- 4.23	- 1.70	- 0.94	- 0.83	- 0.19	+ -0.0

(1) Fe Catalysts - General (Cont'd.)

Note: That the equilibrium is favored by lower temperature and that the lower boiling hydrocarbons are more likely to be formed at higher temperature.

Another fact which should not be overlooked, is the effect of feed gas composition on the equilibrium. This effect is much greater at the higher temperature and may afford a means to direct the synthesis more efficiently.

The data below are shown to indicate the effect of temperature on the susceptibility to changes in feed gas competition. The figures are % yield, based on CO fed for the reaction with n=8 (Octane) at equilibrium, 1 atm. and 349° C.

Feed gas:	Equivalent 1:2 ($CO:H_2$) "ideal"	68.3%
	13.8% N2 Inert	62.9
	Steam: ½ part/1 part CO	54.7
	Steam: 1 part/1 part CO	41.6
	* Excess hydrogen: 5.9%	71.0
	* Excess Carbon monoxide: 17-7%	57.7%
	* (Over the ratio 1:2 $CO:H_2$)	

On the other hand the corresponding figures for 180° C and butane as the product vary only between 99.42 and 99.69%. The results of the operation depend on many other conditions besides the equilibrium, as shown above, but the effect of temperature in this connection is quite evident.

The following sections report in condensed form the work done by German research on the development of iron catalysts.

(2) Lurgi Gesellschaft fuer Waermetechnik. Lurgi had developed an iron catalyst which was supposed to yield a better (more olefinic) gasoline and would be more rugged than the cobalt type. They also had developed a catalyst, which would be used in a once-through operation, for use in city gas plants to convert the CO in the coke oven gas to CH_4 and hydrocarbons. This would detoxify the gas and at the same time enhance its heating value.

There actually was a unit of this type in construction (city gas plant at Leipzig). It was however of the cobalt type since the gas net of that city was operated at LP. The $CO+H_2$ content of the feed gas was low and thus a very active catalyst was required but as complete conversion is not of great importance, a space velocity of approximately 200 at 250°-270° C was used.

(2) Lurgi Gesellschaft fuer Waermetechnik.(Cont'd.)

For operation with their HP gas producer, Lurgi had used an iron detoxification (CO conversion) catalyst of the following compositions:

Fe 100 pts.	Al_2O_3 9 pts.
Cu 10 pts.	Kieselguhr 120 pts.

Lurgi proposed to use 2 types of iron catalysts. One was precipitated on silica and operated at low temperatures (230° C). This catalyst was designed to give a maximum of high boiling product through polymerization. Its composition was as follows:

Fe	100 pts.
Cu	25 pts.
Al	9 pts.
SiO_2	20-30 pts.

This catalyst is quite active as a cracking catalyst and hence must be run at low temperature.

A condensed flow chart giving process data is attached to this report Lurgi drwg: DS am 103.

The second Fe catalyst was proposed for the production of the maximum amount of gasoline and olefines. The operation required for this catalyst is practically the same, except for the substantially higher temperature. The catalyst is very cheap, being made from Lauta-Masse, a product obtained in the manufacture of aluminum from bauxite. The Lauta-Masse is soaked with $CuNO_3$, the copper is then precipitated with K_2CO_3 on the carrier and reduced in the conventional manner.

The operations proposed for wax production and for olefine production are compared in the table below: (See also reference I(c)5 at end of this section).

Basis: 1000 m^3/hr. fresh feed gas/ 10 m^3 catalyst volume:

	Wax Plant	Gasoline Plant
Catalyst	Precipitated (Fe, Cu, Al)	Lauta-Masse(Cu impreg-nated
Pressure	20 atm.	20 atm.
Temperature	230° C	275° C
Processing	2-stage "Kreislauf" in 1st stage only	1-stage with "Kreislauf"
"Kreislauf" gas volume	2500 m^3/hr.	3000 m^3/hr.
Tailgas	480 "	505 "

(2) Lurgi Cesellschaft fuer Waermetechnik (Cont'd)

	Fresh Feed	Total Feed (1 stage)	Tailgas	Fresh Feed	Total Feed	Tailgas
CO_2	5.8	22.9	28.2	2.8	31.5	48.0
Cn Hm	-	1.4	1.9	-	1.3	2.2
CO	37.6	26.9	22.6	53.2	29.8	16.7
H_2	48.1	31.8	17.0	35.6	19.8	11.3
CH_4	0.1	2.0	2.7	0.1	3.5	5.3
N_2	8.4	15.0	17.6	8.3	14.0	16.5

Yield/m^3 ideal gas:

FT liquid	146 gm	98 gm
Gasol	15 gm	32 gm
Alcohols	9 gm	5 gm
	170 gm	135 gm

Product distribution:

Gasoline 200° EP	20%	71%
Kogasin 200-320° C	20%	20%
Soft wax - 320° C	15%	9%
Hard wax - 460° C	45%	
Total Liquid	100%	100%

Olefine Content:

Gasoline	60%	75%
Kogasin	45%	60%

These data are based on pilot plant runs and may be considered somewhat optimistic. Note that "Kreislauf" is employed in similar manner as for the MP cobalt operation. Since the catalyst consumes CO-H_2 in the overall ratio of watergas, no intermediate H_2 addition is required.

Note: That while over cobalt the recycle actually increases CO: H_2 ratio it does not increase the CO_2 content, since little CO_2 is formed over cobalt. In the case of iron however, the use of recycle implies a very high concentration of CO_2 in the feed of the first stage. Hence the shift reaction is impeded and the CO_2 formation is accordingly suppressed.

It is not proposed to regenerate the Fe catalysts. Their life is expected to equal or exceed that of cobalt. The Fe catalysts, according to Lurgi, are just as sensitive to sulphur poisoning as cobalt. Once 3% S

(2) Lurgi Gesellschaft fuer Waermetechnik (Cont'd.)

(wt. on Cat.) is absorbed, the catalyst has lost its activity. For a four month life the feed gas should not exceed 0.3 gms/100 m^3. Gum forming constituents in the synthesis gas, a frequent cause of trouble in FT units, are of course the same danger on Fe as on Co.

Oxygen up to 0.2% vol. in feed can be tolerated (possibly more; Lurgi have no data on this).

Nitrogen is considered a poison, as well as NH_3, which should be removed.

(3) K.W.I. (Kaiser Wilhelm Institut, Muelheim) (See reference I(b)/6 and I(b)/7 at end of section). KWI developed a precipitated Fe catalyst using no carrier. The Fe is precipitated as hydroxide from its nitrate solution, washed, filtered, and pressed. In some cases it may also be alkalized. (For exact recipe see below).

It was found that reduction with H_2 reduces the Fe_2O_3 to Fe_3O_4, which does not yet catalyze the FT reaction. Treatment with CO however, gives a highly active catalyst, following the formation of the carbide. This process ("Formierung") must be carried out under very definite conditions.

It was found that operation with high CO/H_2 gas at atmospheric pressure damaged the catalyst. While at higher pressure no such effect could be established. From this it was concluded that the overcarbidization ("Uebercarbidierung") at low pressure was due to the low H_2-partial pressure resulting in a lowering of this hydrogenating activity of Fe.

It was also found that the pressure at which the formation of the carbide takes place has an appreciable effect on the life and sustained activity of the catalyst in subsequent MP synthesis. Influence of pressure during formation on subsequent activity is shown below:

Pressure during Carbidization	Contraction of Synthesis.
9.0 at press.	5%
3.0 "	12%
1.0 "	28%
0.1 "	30%

Thus a low pressure appears essential for the formation of an active carbide which will retain its activity for many months.

(3) K.W.I. (Kaiser Wilhelm Institut, Muelheim)(Cont'd.)

It was also found that for this formation of an active catalyst an optimum temperature exists (other conditions being equal) near 315° C. With lower temperature the activity is definitely inferior, and with higher temperature only a fair activity results.

Extent of "Forming." Aside from temperature and pressure, the space velocity and duration of the forming are also important. Since the reduction and carbide formation, result in the formation of CO_2 this affords a means to control the forming of the catalyst. The latter is considered terminated when CO_2 in the exitgas has passed through a maximum and reached a constant value. Further production of CO_2 then corresponds to deposition of free carbon.

The importance of this forming can be seen from the variation of the subsequent synthesis temperature required for maximum contraction. An Fe catalyst which was put into operation at 15 atm. without "preforming" required initially 290° C for a 45% contraction. At the end of the 5th month this temperature had to be raised to 300° C. A similar catalyst, "formed" 24 hours with CO at 1/10 atms. and 255° C, was started at 250° C and at the end of the 16th month gave a contraction of 50% at 260° C.

Summarizing the "Forming" it consists in treatment of the catalyst at pressures below and temperatures above those used in the subsequent synthesis. It is preferred to "form" with pure CO at high space velocity. During this treatment a certain equilibrium is established between the solid phase and the gas phase. The lower the CO_2 content of the gas used in formation, the better the reduction and carbide formation.

Some work was done on the analysis of these Fe catalysts. In particular magnetic measurements are used to determine the extent of the conversion from Fe_2O_3 to Fe_3O_4 to Fe_3C. Two Curie points are involved in these changes which allow a determination of the conversion by comparison with known mixtures using a calibrated apparatus. There are probably many carbides present in the catalyst which make an exact determination of Fe_3C difficult. Furthermore it is probably the loosely bound carbon in the higher carbides which accounts for the activity of the catalyst. However, KWI found their method of determining Fe_3C a good way of predicting the activity of a catalyst. There seems to be about 70-80% Fe_3C in a good, well formed catalyst after prolonged use. After an initial complete carbidization the Fe_3C content is reduced to this figure and remains constant at this level. The deposition of free carbon on the catalyst is not considered a "poisoning" of the latter, but simply a mechanical disability.

(3) K.W.I. (Kaiser Wilhelm Institut, Muelheim)(Cont'd.)

The Influence of Alkali on the Catalyst. Alkali was found to increase production of higher boiling hydrocarbons as follows:

Alkali	C_3 g/m^3 ideal gas	Wax %	Liquid HC's %	C_{3+4} %
None	140	13	67	20
1/4% K_2CO_3	148	26	56	18
1.0% K_2CO_3	157	42	47	11

The % alkali is wt. % K_2CO_3 based on Fe. metal. High alkali, however, shortens the life of the catalyst.

Addition of Kieselguhr. Contrary to the experience with cobalt, it appears that Kieselguhr is not required for Fe catalysts. The best results were obtained without a carrier.

Treatment with Hydrogen. It has already been pointed out, that the use of H_2 instead of CO for the "forming" of the catalyst gave poor results.

However, intermediate regeneration over the life of the catalyst gives an immediate but short lived increase in activity. The situation is similar to that encountered with cobalt. The regeneration must however be carried out before the contraction has dropped below 45-50%.

Preparation of Catalyst. A hot solution of iron nitrate is precipitated with soda. It was found that a mixture of ferrous and ferric nitrate gave the best result, pure ferric iron was not satisfactory, with pure ferrous an intermediate.

Copper may be added (½% based on Fe) to give a more reproducible result. The precipitate is washed free of alkali, then slurried in a potash solution, filtered, dried and pelleted. Next the catalyst is "formed" in the manner described above and finally purged with CO_2 for transportation. It is also possible to soak it in wax. The particles are thereby covered and can be exposed to air without losing their activity.

The finished carbided catalyst contains 50 g Fe metal in 100 cc Catalyst. The Fe represents about 60% of the total weight.

Products. The chief characteristic is the olefinicity of the product. The C_3-C_4 cut contained around 70-80% olefines; gasoline (200° EP), 50-60% olefines; diesel oil 10-20% olefines. The wax is practically olefine free.

(3) K.W.I. (Kaiser Wilhelm Institut, Muelheim)(Cont'd.)

The olefines and paraffins are mostly normal hydrocarbons. Overall, about 1 carbon atom in 30 is tertiary. Diolefines are absent.

Oxygenated products are characteristic by-products of the Fe synthesis. The yield was given an approximately 13 g/m^3 water soluble products. Aside from alcohols, which are the bulk of the oxygenated products, the usual mixture of acids, esters, aldehydes was found, but it appears that not much work was done by KWI on this phase of the process. The oxygen content of the hydrocarbon phase was given as 0.2 to 2% with most of the oxygenated compounds in the low boiling fractions.

It was found that these Fe catalysts would produce some very high boiling alcohols (with chain length similar to those of waxes) if operated at 50 atm., or higher, but the yields are low and the catalyst has a tendency to form carbonyl at these pressures.

Summarizing the results of KWI work on Fe catalysts it may be stated that a catalyst and a mode of operation was found which gave the following operational results:

Yield: C_{3+}, single stage	130-160 g/m^3 ideal gas
Catalyst life (without any regeneration)	18 month maximum
Pressure	15 atm.
Temperature	250° C
Space velocity	400 liters gas/Kg Fe (200 VHV)

For best results the feed gas preferably contains an excess of CO over hydrogen but this is not a necessity.

It might be mentioned that Kreislauf operation was not considered favorably here. It was felt that the cost was not justified by the increase in olefines available over a once-through basis.

(4) Rheinpreussen.

The work done by this organization was somewhat similar to that done by KWI. Here too exact studies of the carbide formation were carried out, and a catalyst based on a cheap raw material for use in liquid phase operation was developed.

(4) Rheinpreussen (Cont'd.)

The reason why iron catalysts do not lend themselves to operation at low pressure is explained by Dr. Koebel (Rheinpreussen) as follows:

The Synthesis of hydrocarbons over elements of the 8th Group is based in part on the competing reactions of carbide formation and carbide hydrogenation. It seems that in the case of iron at atmospheric pressure the carbide formation is faster than the hydrogenation. At least a minimum partial pressure of hydrogen is apparently required to hydrogenate the carbides as they are formed and thus keep the active points of the catalyst free for further carbide formation. If the H_2 partial pressure is below the minimum, the catalyst soon becomes "carbided" and loses its activity. This limiting pressure seems to be H_2= 0.5 atm. At one atmosphere starting with water gas and at CO conversion of 60%, the P_{H_2} in the tail-gas is below this figure. At 10 atm. operation, however, under equal conditions, the P_{H_2} in the tail-gas is 3 atm.

It follows that the ability to form carbides does not increase with pressure at the same rate as the ability to hydrogenate. This drawback may, however, be overcome by a treatment of the catalyst, consisting in a formation of carbide at normal pressure, before starting operation at elevated pressure. This procedure was recommended by both Rheinpreussen and the KWI group who had reached the same conclusion independently from each other.

The carbide is formed during the synthesis, if no special "forming" precedes it, but the formation is slow and may not lead to the same carbide since it is formed under different conditions.

Fe_3C is the more desirable catalyst. As the catalyst ages it changes. If the Fe_3C content could be kept up, the activity would remain indefinitely. It may be possible that higher carbides such as Fe_2C are even more desirable but they are difficult to prepare and are unstable.

There is no better means to determine the carbide in a catalyst than magnetic measurements although hydrogenation could be used to determine the "C in Carbide."

Rheinpreussen also studied the effect of alkali on the formation of carbide. Pure Fe_2O_3 was treated with CO to yield carbide, and gave a certain "C in Carbide" value. Upon addition of 1% K_2CO_3, the "C in C" increased by 30% but upon further addition (i.e., 10% K_2CO_3), the "C in C"

(4) Rheinpreussen (Cont'd.)

decreased to 25% below the value of pure alkali free Fe_2O_3. The effect of alkali on catalyst activity is in proportion to these figures.

Copper is frequently added to Fe catalysts. Copper was also found to slightly increase the carbide formation. This is explained by the fact that Cu increases the rate of reduction of Fe_2O_3 to Fe which must precede the carbide formation. This could be interpreted as a confirmation of a statement by Lurgi that copper does not seem to have a catalystic effect in itself but helps in reproducing a catalyst of constant activity. 1% Cu based on Fe is sufficient for this purpose.

Another catalyst was developed by Rheinpreussen using Luxmasse as raw material and adding 0.15-5.0% K_2CO_3 and 0-3.0% copper. A catalyst of this type was kept in operation for 32,264 hours ($3\frac{1}{2}$ years). At the end of that period the catalyst supposedly gave 85% conversion at a space velocity of 80 V/H/V and 113 g. liquid product/m^3 ideal gas, plus 32 gm C_3+C_4. These figures were taken from the monthly reports of the Rheinpreussen laboratory but the data presented there were rather incoherent and must therefore be used with care.

(5) Ruhrchemie.

The long experience of RCH with cobalt catalyst operation led them to develop catalysts containing Fe precipitated on a carrier. Their objective shifted from time to time to Fe catalysts for olefine production, for wax production, or for catalysts to replace cobalt in existing FT units. RCH succeeded in developing a good Fe catalyst for wax production which would be operated at exceptionally low temperatures, but the olefine producer did not get beyond laboratory stage.

During the regular FT meeting at Essen in September 1940, Dr. Roelen gave some information regarding the RCH work. Their findings are generally in good agreement with those of other laboratories. The main difference according to RCH of Fe versus Co is the lower hydrogenating capacity of Fe. This results in 3 important advantages.

(a) There is less CH_4 formed despite the fact that all Fe catalysts require higher temperatures than cobalt.
(b) The products are more olefinic.
(c) Fe can consume CO and H_2 over a much wider range.

(5) Ruhrchemie (Cont'd.)

The first advantages allow a variation of operating conditions over a much wider range than cobalt with corresponding varying boiling ranges of the product, without lowering conversion or increasing methane.

The second is obvious as olefines are a very desirable product (for lube oils and Oxo-synthesis).

The third allows the use of straight watergas without shift.

RCH claim, they can start an Fe catalyst by different methods, such as H_2 reduction, watergas reduction or CO reduction. But it appears that here too the "forming" of the catalyst, the formation of the carbide must precede the actual synthesis.

In accord with KWI, it was found that addition of alkali (in very small concentrations) had a decided effect on the boiling range of the product. The following data were given:

Basis: atm. watergas, 245° C.

Alkali content	Gasoline	Kogasin	Softwax	Hardwax
Fraction	-200° C	200-320°C	320-460°C	460° C
0.0 - 0.25% KOH	58.5%	24%	14%	3.5%
3% KOH	20.5%	13%	16.5%	50%

While it is possible to vary the results with small changes in catalyst composition without any change in the operation, it is also possible to vary the operating conditions using the same catalyst and thus obtain varying results. For example, an increase in pressure raises the boiling range (same as over cobalt), all other conditions being equal:

Pressure	1.0	5	20 atm.
CO conversion	95	70	75%
Yield gm/m^3 ideal gas	90	86	120
Gasoline %	57%	30%	22%
Kogasin %	24%	25%	22%
Wax %	19%	45%	56%
Olefine in gasoline	68%	63%	63%
Olefine in Kogasin	41%	49%	46%

For a proposed commercial operation to give maximum wax production, the following data were given by RCH. The catalyst is a ppt'd Fe cat:

(5) Ruhrchemie (Cont'd.)

Gas	Watergas	38% CO	48% H_2	(1:1.26)
Pressure	15 atm.			
Temperature	230° C			
Contraction	60%			
CO conversion	80%			
CO to CO_2	25.6%			
CO to CH_4	7%			
H_2 conversion	80%			
$CO+H_2$	80%			
Consumption CO:H_2	1:1.24%			

Yield g/m^3 Feed gas	1 stage by test	2 stage calculated	Total
C_3+C_4 (Gasol)	10	3	13
Liquid products	135	20	155
	145	23	168

Product distribution:

Gasoline	200° C EP	16% wt	70% olefines
Kogasin	200-320°	20% wt	
Soft wax	320-460°	22% wt	
Hard wax	460°	42% wt	

This described catalyst was to be used for production of wax. If olefines were the main objective of the synthesis, the same catalyst with a higher Kieselguhr content was used. As much as 10 m^3 of the wax catalyst had been prepared in pilot plant operation. The following information was obtained regarding the preparation of this catalyst:

The iron is dissolved to give a solution of Fe $(NO_3)_2$ (non-ferric Ion), Cu is added as well as Ca $(NO_3)_2$ with Fe: Cu: Ca in the proportions 100 - 15 - 5. The metallic nitrates are precipitated as carbonates by pouring the hot solution into a solution of hot soda. The endpoint of the precipitation is at 6.6—6.8 pH. At the end of the precipitation Kieselguhr is added and the batch is filtered. The cake is washed free of NO_3 (0.4%, Na NO_3 on 100% Fe is maximum), is then slurried in a 20g/lit. KOH solution and again filtered, dried and formed.

The catalyst is next reduced with a mixture of $H_2:N_2 = 3:1$ using a space velocity of 3000 V/H/V in an analogous manner to cobalt catalyst.

(5) Ruhrchemie (Cont'd.)

The reduction is carried out with hot gas (300° C). As soon as the catalyst has reached this temperature the reduction is complete (3/4 hour).

The reduction occurs in steps from $Fe(OH)_3$ ---------- Fe_2O_3 -------- Fe_3O_4 -------- FeO -------- Fe. With the stages overlapping, the several oxides are present in the final product. A good catalyst should, in fact, not contain more than 5-8% Fe-based on the total iron present. The value of "total reduced iron" ("Reduktionswert") was used to control the reduction. It should not exceed 65-75%. This value is determined by using 2% acetic acid. The catalyst is cooked 1½ hours in an excess of this acid. Fe and FeO dissolve, the remainder represents the unreduced iron oxide.

In starting a new batch, the catalyst is operated using watergas at minimum pressure at 130° C for ½ to 1 day. Following the "forming" the temperature and pressure are raised to operating level. The CO_2 usually added before shipment must be added very carefully to avoid overheating, since the heat of adsorption is very high.

The wax yield over this cycle depends largely on the proper KOH content (3.0%) of the fresh formed catalyst. The operating conditions for wax production are identical to those given under Lurgi Kreislauf operation and may be noted there.

(6) Brabag.

The entire research and commercial installations of this company connected with FT work are located at Ruhland-Schwarzheide and were not available to the members of this investigating team. No first-hand information regarding their development was obtained.

It is however known that Brabag had developed Fe catalysts. The catalysts are of the precipitated carrier type. Watergas was used and consumed in the ideal ratio. With this gas a three month catalyst life was obtained. The catalyst had to undergo "forming" which required 3-4 days with a space velocity of 10 V/H/V.

I.G. FARBENINDUSTRIE A.G.

I.G. had done considerable work on Fe catalyst prior to 1938 and a good part of this work was made available during the USAC meeting in 1938.

I.G. Farbenindustrie A.G. (Cont'd.)

The work was carried out separately in Leuna and Ludwigshafen. The Leuna group, headed by Dr. Herold, deviated from the Fischer-Tropsch Synthesis and developed the Synol process for the direct production of alcohols. In Ludwigshafen, Dr. Michael (under Dr. Pier) continued work on gas recirculation and liquid phase operation while Dr. Duftschmid (under Dr. Mueller-Conradi) also developed a liquid phase process. Dr. Scheuermann worked on precipitated Fe catalysts.

I.G. had also worked on cobalt catalyst prior to 1939 but apparently only to substantiate Ruhrchemie's claims. Even at the present time, the I.G. Oxo-synthesis was based on the standard cobalt catalyst of RCH.

In the iron field, however, I.G.'s work was original, particularly their work on fused and sintered catalyst of the ammonia type, with which I.G. had some 25 years of practical experience. It has been claimed that such catalysts cannot possibly be as active as the precipitated type and thus had to operate at higher temperatures. Nevertheless I.G. was able to use their "WK 17", a sintered catalyst in the synol process, which operates at very low temperatures.

I.G. has done much work to develop methods for carrying out the synthesis in systems other than the plate or tube type reactors. None of these processes had reached commercialization. This may be due to the war and to the fact that I.G. with their high pressure hydrogenation had found better means to produce high quality motor and aircraft fuels and thus had only limited interest in the process.

The Synol unit, however, had been developed to a point where construction of a large plant had actually been decided upon. This is described in Section II, of this report.

(7) I.G. Farben Leuna.

Contrary to I.G.'s work on cobalt catalysts there were not many detailed catalyst studies made on iron catalysts. The effect of variations in operating conditions as studied on a number of Fe catalysts particularly the regular ammonia catalyst used in this plant. The influence of the temperature of reduction was studied on a fused iron ammonia type catalyst. The operating conditions in each case were identical, using watergas as feed.

(7) I.G. Farben Leuna (Cont'd.)

Reductions carried out with hydrogen at 1 atm. and 100 V/H/V.

Temperature of Reduction	Length of Reduction	Yield
850° C	16 hours	63 g/m^3 ideal gas
500° C	10 days	79 "
450° C	11 days	102 "
420° C	4 days	105 "
400° C	10 days	105 "

At lower reduction temperatures the activity rises, with a special sharp increase near 500° C. The extent of reduction (calculated from the water formation) is apparently only a secondary influence. If the H_2 is carried out at elevated pressure, the reduction can be completed even at low temperatures (200 atm. H_2, 300° C, 40-60 hours)

In accordance with all other observers, it was found that increased space velocity and higher temperatures in the synthesis increased the yield of lower boiling products. The reduction temperature, however, influenced the spectrum of the product differently, i.e., low reduction temperature gave low boiling products (all other conditions being equal). It appears that the reduction at lower temperature increases the hydrogenation capacity of the catalyst, which in turn increases the production of low boiling products.

The effect of space velocity was studied using a 15 mm. diameter tubular reactor. Space velocities (VHV) from 100 to 600 were used with 400 V/H/V determined as the practical limit. At higher velocities the catalyst had tendencies to coke-up (by CO decomposition) due to local overheating. By taking good care, 500-600 V/H/V were reached for limited intervals. The actual overheating of the catalyst due to the high load is considered the cause of the increase in light products. With higher temperature and higher space velocity, somewhat more branched hydrocarbons were produced but the effect was not very pronounced.

The kinetics of the FT synthesis were formulated by I.G. chemists as follows:

(a) $CO + 2H_2 \longrightarrow CH_2 + H_2O$ Formation of methylene
By way of carbide formation and hydrogenation of the carbide.

(b) (1) $n\ CH_2 \longrightarrow (CH_2)_n$ polymerization of methylene

(2) $CH_2 + H_2 \longrightarrow CH_4$ Hydrogenation of methylene

(7) I.G. Farben Leuna (Cont'd.)

(c) (1) $(CH_2)_n + H_2 \longrightarrow C_n H_{(2n+2)}$ Ending of polymerization due to hydrogenation of olefine.

(2) $CH_3(CH_2)_{n-3}CH=CH_2 \longrightarrow CH_3(CH_2)_{(\frac{n}{2}-2)}CH=CH(CH_2)_{(\frac{n}{2}-2)}-CH_3$

Ending of Polymerization due to shifting of double bond to middle of molecule.

It is obvious that the composition of the final product depends on the relative velocities of these reactions and thus on the relative rates of change of these velocities with change in temperature. It should also be noted that iron catalysts have apparently a good activity corresponding to reaction (C)(2).

Another reaction, not shown here but of interest would be the isomerization to branched chain hydrocarbons. The ability to catalyze this reaction is unfortunately not too good.

It was found that structurally there is little difference between gasoline synthesized over iron and over cobalt. The first gave much more olefines, but upon hydrogenation both gasolines showed the same octane number.

It is still possible to find two "Fe gasolines" with the same olefine content which differ in octane rating due to shifting of the double bond. It may be possible to develop a better control of these different reactions and thus produce a product of substantially only one type of hydrocarbon. Lastly there is still another reaction which is apparently the basis for the Synol process, i.e.; the saturation of the terminal double bond with H_2O to form an alcohol. The process is described in Section II.

Carbon deposit is a well known occurence over Fe catalyst. It is due to the fact that Fe catalyses the reactions.

(a) $2\,CO \longrightarrow CO_2 + C$

(b) $4\,CO + 3\,Fe \longrightarrow Fe_3O_4 + 4\,C$

I.G. checked this by determining the ratio Fe/Fe_3O_4 in a new and coked Fe catalyst. The ratio had shifted toward an increase in Fe_3O_4. In X-ray photographs the carbon did not appear indicating amorphous carbon. The newly formed Fe_3O_4 is very finely divided compared with the large crystals of Fe_3O_4 in the fresh catalyst.

(8) I.G. Farben-Ludwigshafen.

Waelzgas Process. (See reference I(b)/8, I(b)/9 and I(b)/10 at end of this section).

The gas circulating process (Dr. Michael) was well known before 1938 and had been discussed with U.S. representatives at the time. Dr. Michael used his sintered catalyst prepared by treating pelleted Fe powder (from carbonyl) with K_2CO_3 solution and sintering in H_2 atmosphere at 800-850° C for 4 hrs. The catalyst was actually iron carbide. But no exact work on the different carbides appears to have been carried on. The catalyst was not active requiring a temperature of 325° C for a 75% conversion.

When it became apparent that the process could not compete with high pressure hydrogenation in the production of high octane gasoline, it was decided to develop a process for the production of chemicals particularly olefines. The sintered catalyst was abandoned and replaced with a precipitated Fe catalyst. This catalyst did not have the mechanical strength required in the "Waelzgasprocess" and the process was abandoned. All further work carried out by Dr. Michael centered around operation in liquid phase and is described in that section.

For ready reference a set of operating data is listed below:

Reactor:	4 m^3 sintered Fe catalyst
Temperature	325° C
Pressure	20 atm.
V/H/V	250
Feedgas	CO: H_2 = 4:5 (17% inert)
Catalyst yield	0.7 Kg/liter catalyst/day

Product Distribution:

C_2H_4	8%
C_3H_6	9%
C_3H_8	3%
C_4H_8	8%
C_4H_{10}	2%
Gasoline 200° C	48%
Diesel oil 200-350° C	14%
Wax	1%
Alcohols	7%
TOTAL	100%

22 pts. of methane-ethane are also formed for 100 pts. of the listed products.

(8) I.G. Farben-Ludwigshafen (Cont'd.)

The gasoline must be refined (dehydration of alcohol) to remove oxygen. This causes about 6% loss. The treatment is carried out at 380° C over alumina. The treated gasoline has a Res. O.N. of 84. The diesel oil is ready for use, cetane number 50-55.

A horizontal reactor has been proposed to carry out the synthesis containing 20 m^3 of catalyst arranged in 4 separate horizontal layers of 250 mm. thick. Two reactors of this type would yield 10,000 ton/year of FT product. Note that this daily production per unit catalyst volume is about three times that reported in commercial FT operation. This is due to the higher space velocity, but the data should be used with caution.

A fairly detailed cost estimate for a 100,000 ton/year plant had also been worked out. The detailed figures may be taken from the attached report by Dr. Michael. The cost figures given are very nearly the same as these listed by Lurgi for a conventional FT plant using Fe catalyst and gas "Kreislauf".

Basis: RM/1 yearly ton total product	Synthesis & recovery	Total Plant
I.G. (Waelzgas unit)	243.-	865.-
Lurgi (Kreislauf)	290.-	590.-

(9) Comparative Tests with Fe Catalysts.

In the above sections, development work on Fe catalysts by different companies has been described. The reader may find it difficult to compare the results of this work, since each investigator is inclined to report in a different manner and also because the main objective of research may have been varied.

Apparently the German government felt the same way. Furthermore, it believed a decision regarding the use of Fe catalyst, at least in the three HP synthesis plants had to be made. To settle the argument, a set of tests in which each participant furnished his catalyst and operating personnel and using the same pressure and temperature was conducted by the government. The tests were carried out in the winter of 1943/1944 at the Brabag plant in Ruhland. (See reference 1(b)/26 to I(b)/33 at end of this section.)

The participants were:

Ruhrchemie	I.G. Farben
Lurgi	Rheinpreussen
Brabag	Kaiser Wilhelm Institut

(9) Comparative Tests with Fe Catalysts (Cont'd.)

Appended to this report is a set of charts giving the operating data of each tests and the comparative yields. In addition, there is a copy of the report of each participant, after completing the test and comparing his own results with that of the others. Little work was carried out after completion of these tests and the results therefore represent the present state of German development of iron catalyst.

Note however that the range of operating conditions were not too wide and better results undoubtedly could have been obtained, if no limitations had been imposed. The arrangements for the tests were as follows:

Each reactor consisted of one double tube containing 4.8 liters of catalyst (O.D. 44 mm. I.D., 24 mm. height 4½ m).

The fresh feedgas (identical for all units) had a $CO:H_2$ ratio 1:1.25 (watergas) and 12% inert. S content under ~~0.1 gm/100 m³~~.

The product recovery was conventional. The analytical methods are described in the attached report. The catalysts used by the participants are listed below. It was of importance to the Germans that the catalyst would be produced in one of the existing plants and did contain a minimum of critical materials, such as copper ("Sparmetalle").

COMPOSITION OF Fe-CATALYSTS FOR "R.A. VERSUCHE"
(All quantities based on 10 m³ Cat. volume)

Catalyst	Fe Ton	Cu Kg	Alkali %	Carrier	"Forming" (Reduction)
K.W.I.	6	60	1% K_2CO_3 Basis Fe	None	Watergas
LURGI	3.9	390	30% K_4SiO_4 9% K_2O Basis Fe	SiO_2 (Waterglass)	Hydrogen 30% reduced
BRABAG	6.9	690	0.5% K_2CO_3 Basis Fe	None	Watergas 245° C H_2 or Sygas:225°
I.G.	18.0 (fused iron)		1% K_2CO_3 Basis cat.	Al_2O_3CaO 2% max.	Hydrogen at 500°C
RUHRCHEMIE	2.5	125	0.5-2% K_2CO_3 Basis Fe	Kieselguhr	Hydrogen
RHEIN-PREUSSEN	2.7	135	0.5-1% K_2CO_3 Basis Fe	Ground Dolomite	Hydrogen 3-400° C Watergas 245° C

(9) Comparative Tests with Fe Catalysts (Cont'd.)

It may be seen that the composition does not vary greatly. Lurgi used a somewhat higher alkali content. At the same time the yield of oxygenated compounds was highest over this catalyst. The catalysts vary however in regard to their apparent density as shown below:

I.G.	2.27	("Schuttgewicht" Kg/lit.cat.vol.)
Brabag	1.37	" "
K.W.I.	1.02	" "
Rheinpreussen	0.68	" "
Lurgi	0.79	" "
Ruhrchemie	0.44	" "

I.G.'s catalyst is fuzed, hence the high density. Brabag and K.W.I. use no carrier, while the three others use different types of carriers. Assuming that Fe is the only really active ingredient, it is of interest to note that the great variance in iron content had but little effect on the space velocity and specific output of the catalyst.

From the attached data sheet it can be seen, that based on 10 m^3 catalyst volume (standard FT reactor), a daily yield of 2.55 tons to 1.93 tons of C_3+ products was obtained by the six participants. This figure compares favorably with LP cobalt operation. The yield based on feed (88% $CO+H_2$) Watergas was from 99.5 to 87.4 g/m^3.

Oxygenated compounds are excluded in these yields. The operating pressure was identical (10 at) in all cases. The temperature and V/H/V were up to the individual operator. At the end of two weeks all units had reached around 220° C. The space velocities varied between 105 to 110 on the average. A summary of the results is listed below:

	KWI	LURGI	BRABAG	I.G.	RCH	Rh. Pr.
GAS (C_1+C_2)	16.6	10.8	8.4	16.8	13.6	17.1
GASOL (C_3+C_4)	19.9	12.3	9.8	18.1	14.3	21.5
GASOLINE (C_5-C_{10})	25.1	19.5	17.9	25.7	22.3	27.8
DIESEL OIL ($C_{11}-C_{18}$)	14.0	13.1	16.4	11.5	12.7	13.7
GATSCH (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 ALCOHOL	6.11	9.2	4.1	7.0	11.3	5.3

(Cont'd)

(9) Comparative Tests with Fe Catalysts (Cont'd.)

	KWI	LURGI	BRABAG	I.G.	RCH	Rh. Pr.
TOTAL ALCOHOL	7.0	14.4	9.5	10.7	15.8	7.5
TOTAL ESTER	1.1	8.0	2.7	1.7	2.6	0.3
TOTAL OLEFINE	25.9	30.4	34.2	39.1	26.1	29.7
Tons/day TOTAL	3.26	3.19	2.88	3.2	2.47	2.6
g/m^3 Sy. gas TOTAL	125.2	124.2	108.3	117.1	103.1	104.0
g/m^3 max. Value	147.3	142	141	144	147	168
CO:H_2 Consumed Ratio	0.80	0.66	0.69	0.74	0.72	1.07 ($CO:H_2$ feed 1:1.25)
CO Conversion	85.0	88	77	81	70	57

The products vary within a reasonable range: Lurgi + Brabag gave the most hard wax, one of the objects of this race. Rheinpreussen produced a very light product, which might be considered a failure. I.G. and KWI apparently produced the most olefines. The gasolines varied only little among themselves and also if compared with an LP cobalt gasoline. (See report of Analysis by KWI). The waxes were tested for their use as feed to oxidation plants. No definite conclusions were reached on the subject but it was feared that the wax paraffins might be too highly branched.

Only three of the six catalysts operated 90 days with the first batch catalyst. The others ran into coke trouble and had to renew the charges repeatedly (4 times in the case of Rheinpreussen), before the required 90 days run could be completed. This was a serious drawback. If the catalyst could not be prepared with sufficient assurance that coke deposit would not occur, it could not be considered ready for commercial application. (Coking of an FT oven is a serious problem requiring a shutdown of several weeks for cleanout).

The important fact about these tests is apparently that all participants obtained reasonably good results, under conditions similar to those used in MP cobalt operation with a set of greatly different Fe catalysts (great difference in Fe content). Another fact is the general use of copper and alkali to promote the catalyst.

(9) Comparative Tests with Fe Catalysts (Cont'd.)

Liquid Phase Operation

The idea of conducting the FT synthesis in liquid phase is not new as it had been attempted a long time ago by Fischer. Today, it is considered as promising and research on the subject was carried out notably by I.G. Farben, Ruhrchemie, and Rheinpreussen. The easier control of the reaction temperature is the main incentive for the use of such a system. The main drawback, if any, is the probably loss in catalyst efficiency, a point which is not yet clear. Three types of operations were tried:

(a) "Oel Kreislauf": The use of a solid catalyst bed with the oil being circulated over the catalyst concurrently with the gas.

(b) "Schaumfahrweise" Suspension of the catalyst in the oil phase and dispersion of the catalyst by the gas using a ceramic disc or mechanical stirrer. The heat of reaction is removed by circulating the slurry through an external cooler.

(c) Static liquid phase: Similar to (b), but the heat of the reaction is removed by a set of cooling tubes which are inserted in the liquid.

Systems (a) and (b) were used by I.G. Farben and system (c) by Rheinpreussen.

(10) "Oilkreislauf" Process - I.G. Farben.

(See reference I(b)/11, I(b)/12 and I(b)/13 at end of this section)

The catalyst used was of the fused iron type (ammonia catalyst). It was obtained by melting pure iron powder (from carbonyl) with O_2 and adding certain promoters. The melt was then broken into particles from 8-15 mm. size and arranged in a reactor as a solid bed. A 500 mm. chamber, 6 m. high was used in the tests.

The oil used for circulation is the product of the synthesis itself, sp. gr. 0.8 - 0.81, conditioned by distillation to keep it within any specified boiling range. The use of the oil prohibits the development of any local hot-spots and thus lowers the yield of gaseous products.

The operating results were as follows:

Pressure	25 atm.
Temperature	300° C (approximately)

(10) "Oilkreislauf" Process - I.G. Farben.(Cont'd.)

Space velocity	200 V/H/V (apparent catalyst density 2.5)
Yield	150 g/m^3 total product/basis ideal gas
Conversion	87%
Output	7.2 ton/10 m^3 catalyst volume.

Product Distribution.

Gasoline	40% (50% olefine, 2% oxygen, ON65)
Gas Oil	20% (40% olefine, 0.6 - 1% oxygen)
Hard Wax	20 (95° C melting point)
$C_3 + C_4$	15 (75% olefine)
Alcohol	5% (mostly ethylalcohol)

Olefines boiling above 100° C consisted of 50% normal and 50% iso-olefine (no data were given for the paraffins).

The most important fact is the high space velocity and resulting high production from a given catalyst volume. It is furthermore a considerably simpler and thus cheaper method, than the customary synthesis.

The cost for a 100,000 ton/year plant was given as RM 5,720,000 (RM 57.2/yearly ton) as compared to RM, 243/yearly ton for the gas circulation process (I.G.) or RM 290/yearly ton for a regular FT plant (Lurgi) with Fe catalyst and "Kreislauf". This figure appears quite out of line. The difference may be due to the exclusion of certain auxiliary equipment.

The use of the "Oilkreislauf" was later considered for the production of alcohols. In particular alcohols in the $C_9 - C_{12}$ range were desired for detergents and chemicals. To this end tests were run with the system at elevated pressures (100 and 180 atm.) but the results were negative since the product was quite low boiling.

(11) "Schaumfahrweise" Process - I.G. Farben.

(See reference I(b)/18 to I(b)/22 at end of this section).
This process was developed by Dr. Michael after abandoning the gas-recycle principle.

It is quite similar to the "Oelkreislauf" process except for the handling of the catalyst. The latter is here held in suspension in the liquid by the gas bubbling up through the reactor. It was desired to operate in a system where the catalyst was dispersed widely and in direct

(11) "Schaumfahrweise" Process - I.G. Farben.

contact with the gas if possible. An attempt to obtain this result by dispersing the gas to give a regular froth was made using the product of the synthesis as liquid phase and forcing the gas through a ceramic disc or nozzles with very fine pores to give the necessary dispersion.

The heat of reaction is removed by circulating the slurry through an outside cooler. For this purpose the reactor is allowed to overflow into the settling vessel where the unreacted gas carrying the light product, vapor is released and withdrawn. The slurry is then passed through the cooler and then picked up by the circulating pump. The net excess product boiling within the range of the circulating oil is withdrawn.

Preliminary tests were carried out in a reactor 500 mm. diameter x 8.0 m. high (1.5 m^3 reactor volume). Some initial difficulties, such as wear in the slurry pump, could be overcome by use of flushing oil in the stuffing box. The oil velocity required for good operation was such as to give 20 changes of oil per hour in the reactor.

Some difficulty was also encountered with the dispersion plate. The feed gas had to be heated to prevent thermal stress and rupture of the disc. A chamotte plate showed good stability. A disc with 0.1 mm. pore size gave good reactor output but resulted in 5 atm. pressure drop. A 0.2 mm. pore size was substituted resulting in a pressure drop of 1 atm. but causing at the same time a drop in output of 25%. Apparently the dispersion depends greatly on the pore size.

No emulsifiers were used in the system but certain of the liquid oxygenated compounds gave such an effect.

In one test the catalyst, after 8 weeks, began to produce increased amounts of low boiling products and less wax. This could have been caused by sulphur, but it could have been due to the extraction of the alkali in the catalyst by the fatty acid formed in the synthesis.

Upon continued operation (3 months) increased losses of catalyst were noted, which could not be explained by the mechanical losses such as pump leaks or entrainment. Upon inspection it was found that the catalyst had formed a solid cake around the wall of the oven (4 cm. thick) particularly in the upper section of the vessel. The catalyst had also settled out in the gas separator. The deposit was thoroughly analyzed and was found to have the following composition: (next page)

(11) "Schaumfahrweise" Process - I.G. Farben (Cont'd.)

$FeCO_3$	48.20% wt.
FeO	13.40 "
Fe_2O_3	0.25 "
Fe_2C	8.50 "
Fe metal	20.30 "
Free carbon	5.10 "
S (Sulfide)	0.03 "
Other	8.81 "
TOTAL	100.00% wt.

The high Fe CO_3 content is due to the high CO_2 content of the exit gas (partial pressure $P_{CO_2} = 6-8$ atm) reacting with FeO. It was further concluded, that some gum-forming substance had served as a glue to hold the catalyst on the wall. Studies to analyze this material were under way

(a) Catalyst.

The catalyst was prepared by decomposing iron carbonyl, 1% alkali was added. After reduction the catalyst was ground in oil to 1-5 m particle size. The concentration in the liquid was 300-400 Kg/m^3.

The catalyst operates at comparatively low temperatures and the amount of gas formed is small. At 70% conversion, the gas analyses are as follows:

	Feed gas	Tail gas
CO_2	0.8%	30.4%
C_mH_{2n}	-	3.0
H_2	42.5	31.1
CO	53.6	27.8
HC^s	1.0	3.7
N_2	2.1	4.0

It is therefore possible to remove the CO_2, and return the tailgas to the reactor without at the same time diluting the feedgas with inert components, thereby the ultimate conversion could be increased to 90%.

The capacity based on reactor volume varied with temperature. For operation at 20 atm. the following figures were given:

Temperature	Space Velocity
250°	80 m^3 gas/m^3 reactor
275°	125 " "

(11) "Schaumfahrweise" Process - I.G. Farben (Cont'd.)

Note: That the space velocity is again in the same range as in ordinary FT operations. For 100,000 ton year primary product, 950 m^3 reactor volume are required according to Dr. Michael corresponding to 2.9 ton/day/10 m^3 catalyst.

PRODUCT DISTRIBUTION

Boiling Range	% Weight	% Paraffin	% Olefine	% Alcohol	% Acid & Ester
1 - 50° C	4	12	85	0	3
50-100°	20	7	83	5	5
100-150°	16	11	67	15	7
150-200°	10	20	62	12	6
200-250°	12	17	63	12	8
250-300°	10	25	54	10	11
300-350°	8	38	45	5	12
+350°	20	-	-	-	-

Note the high content of olefines and oxygenated compounds.

For commercial practice a 12-15 m^3 oven was considered practical. No plant costs had been calculated for this type of unit but for a 100,000 T/year plant the following utilities were required. (This includes complete plant and product recovery).

Steam	12.5 ton/hr.
Water	3500 m^3/hr.
Power	3120 KW
Fuel	2 x 10^6 K cal/hr.
Labor	71 men/shift.

(b) Products.

The high olefine content makes the product suitable for chemical synthesis. The C_3 - C_4 fraction may be polymerized.

The gasoline can be refined for removal of oxygenated products in the conventional manner of bauxite.

Octane rating of treated gasoline:	70 (Research) for 250° temperature. 75 (Research) for 275° Synthesis.

(11) "Schaumfahrweise" Process - I.G. Farben (Cont'd.)

The removal of oxygenated compounds is an important step if the fractions are to be used for polymerization (with $AlCl_3$) or for the Oxo process

The middle oil has a cetane number of 70 and may be used directly; but it is of course the preferred feed for lube oil synthesis and the Oxo reaction.

The wax may be cracked to give a 70% yield of olefinic middle oil. Before it can be used for oxidation it is necessary to hydrogenate the olefines and at the same time remove the higher alcohols and esters.

About 70% of the total wax is hard wax with a melting point over 80-90° C.

(12) "Static Liquid Phase" Rheinpreussen.

Aside from I.G. Farben the attempt to operate in liquid phase was also made by Rheinpreussen. Their work on liquid phase operation did not leave the laboratory stage. The reaction was studied on a small scale and appeared quite successful. A pilot plant was designed employing a new type of reactor and the unit had been assembled for the most part when the progress of the war stopped further work.

The system employs a slurry of catalyst in the reaction products, the catalyst being held in suspension by the rising bubbles of the feedgas. Contrary to the Michael process the slurry is here not circulated through a cooler but forms a static layer. The heat of reaction is removed by a cooler consisting of a multitude of tubes hung vertically in the reactor. The details are described in the following section of new reactor design.

The net product of the synthesis boiling within the range of the slurry oil would have to be withdrawn from the reactor and filtered to remove the catalyst. This filtration problem has been the subject of a special study carried out by Rheinpreussen.

The catalyst in these studies was prepared from Luxmasse (the same material as is used for the "Grobreiningung". The raw mass is thoroughly washed with water and then alkalized with K_2CO_3. Finally the catalyst is ground in Kogasin to give a fine suspension. The density was around 7 g Fe in 12 liter suspension (3.5% slurry). Here too it was found that the K_2O content of the catalyst apparently dropped during operation. It was attempted to correct this by adding K_2CO_3 in powder form to the slurry, but without success.

(12)"Static Liquid Phase" Rheinpreussen (Cont'd.)

After a certain time the catalyst slurry was withdrawn, filtered, and the wax extracted, but this treatment also seemed to have little effect.

Other catalysts, with and without carrier were studied in this system. Carriers appeared to give a lower boiling product, no wax. In one case no liquid buildup was noticed for a period of 670 hours.

Before putting such a unit on stream one of the main problems is the necessity to keep the slurry from settling. It may be necessary to use N_2 or CH_4 to do so before the synthesis gas is admitted.

The following results were given for operation with slurry catalyst in the laboratory.

Feedgas	CO = 40%; H_2 = 44%
Forming of catalyst	(a) Heating slurry (with N_2 flowing) to 278° (b) Form with CO containing gas at 250° for 10 hrs. (c) Put on stream: rate 6 lit/hr feed/10 g Fe.
Conversion	94% CO
Absorber 60° C	12 gm/m^3 CO+H_2
Light oil 60-280°C	38 "
Heavy oil 280° C	65 "
C_3+C_4	9 "
CH_4	2 "
	126 gm/m^3 CO+H_2

This operation appears of great interest and it was regarded as highly promising by the Rheinpreussen engineers.

(a) Ruhrchemie.

Ruhrchemie had done some work on liquid phase operation early in the war. The work apparently had not reached the stage of large scale pilot plant operation. A patent had been applied for operation in liquid phase on 10 March 1941.

According to this claim the operation was to be carried out by passing the feed gas through a catalyst slurry. RCH considered it essential to operate at high space velocity, about 200-700 V/H/V. Under these conditions the conversion was around 50%. This led to the use of a multistage process. The conversion was in fact governed by the amount of CH_4 formed in the synthesis. A maximum of 1% CH_4 formation was to be allowed in each stage.

(12) "Static Liquid Phase" Rheinpreussen (Cont'd.)

The underlying thought is the assumption that in all liquid phase operations the higher boiling products are in danger of being cracked due to the much longer contact with the catalyst. Not enough practical experience on liquid phase operation is available as yet to study this effect.

Another RCH patent application dated 7 July 1941, was supposed to cover operations with liquid injections as means to remove the heat of reaction. This operation also is not new, but was not carried out in any large scale apparatus. The injected liquid is evaporated and the quantity used in such that the heat of reaction balances the latent heat of the injected liquid. It appears that the quantity of liquid required might be quite substantial and RCH visualized a stepwise operation with condensation between each stage.

No operating data on RCH liquid operation were obtained.

(13) New Reactor Design - General.

There has been practically no new development in this direction that has reached commercial application with the exception of the "Taschenrohr" oven at Krupp's plant in Wanne-Eickel.

All existing LP plants use the standard plate-oven. The MP plants employ the double tube reactor which has been described in detail in the literature, and at Schaffgotsch some single tube reactors were used. However, parallel with the development of the Fe catalyst, there were attempts to improve the reactor.

The following improvements are noted:

(a) Krupp Taschenrohrofen.
(b) Lurgi MP reactor.
(c) I.G. MP reactor (for Synol plant).
(d) Rheinpreussen liquid phase reactor.

Empty vessels as are required in the I.G. "Waelz" or "Oelkreis" process are not considered here.

(a) "Taschenrohrofen". (See reference I(b)/39 at end of this section).

This oven is a regular MP Fischer oven. Instead of using the conventional double tubes, the tubes are large and contain a number of internal

(13) New Reactor Design - General (a) (Cont'd.)

tube fins, which intersect the tube in such a manner that no catalyst particle is more than 5 mm. from the nearest fin or tubewall. 16 ovens of this type were installed in the 2nd stage of the Krupp plant at Wanne-Eickel. (There were also 8 regular double tube ovens in the plant).

A detailed drawing of the oven is attached. Each tube 75 mm. diameter and 3750 mm. long, contained 0.01275 m^3 of catalyst, the entire oven contained the conventional 10 m^3. The watercooled surface is 0.85 m^2/tube (670 m^2/oven). The finned surface is 2.13 m^2/tube (1670 m^2/oven.)

It was stated that the catalyst was not easily removed from these tubes. The capacity of the oven as a unit was comparable to the double tube oven.

(b) Lurgi M.P. Oven. (See reference ~~I(b)/42~~ at end of this section).

The use of Fe catalysts required the construction of ovens which could stand the 20-30 atm. pressure on the catalyst side and at the same time the somewhat higher pressure on the steam side (up to 60 atm). The arrangement proposed by Lurgi consisted simply of the conventional LP plate oven installed on a horizontal HP drum. One head of the drum is flanged and the cooling coil is connected to that head. For filling and removal of the catalyst, the flange is opened and the head with the entire catalyst and cooling system is drawn out of the pressure drum.

The plate bundle itself is enclosed in a thin sheet jacket to prevent flashing of the pyrophoric catalyst, when the bundle is drawn. The same difficulties in filling and removing of catalyst usually experienced in the LP oven will have to be met in this design.

A pilot unit of this type, containing 7 m^3 catalyst and operating at 20 atm. was installed at the gasworks near Boehlen-Rotha. The unit was to be studied for possible use in detoxification of city gas (and of course, FT). Only one run had been made at the unit and the oven apparently performed well. No detailed operating data were available, but the pilot unit had been designed to operate at space velocities up to 400 V/H/V (including recycle gas). The gas enters the top of the basket containing the catalyst and passes down through the bed. The bottom of the basket is connected to the exit nozzle of the pressure vessel by means of a special expansion joint.

(13) New Reactor Design - General (Cont'd.)

(c) I.G. Farben Synol Reactor. (See reference I(b)/41 at end of this Section).

This oven was developed to carry out FT reactions and related synthesis. Considerable work was done by I.G. engineers to arrive at a theoretical basis before selecting a reactor for these exothermic reactions. Three possible arrangements were considered. (See report by Dr. E. Wirth of April 1942, Leuna., Reference I(b)/34 to I(b)/37 at end of this section).

(1) Catalyst inside the tubes.
(2) Catalyst between plates.
(3) Catalyst outside the tubes.

The following general conclusions were drawn:

(a) The catalyst in tube arrangement required the largest cooling surface and, based on total reactor-volume, contains the least amount of catalyst. But it may be arranged to give tall catalyst layers should that be required.

(b) The catalyst outside the tubes is superior to the reverse arrangement and the improvement becomes greater as the diameter of the cooling tubes decreases. Structural difficulties apparently are the main drawback

(c) The plate reactor is also superior to the catalyst tube reactor. But for increased heats of reaction (or better for increased heat release per m^3 of reactor), less control is afforded by the plate oven, as a substantial temperature gradient develops across the plate.

These conclusions may be only of theoretical interest and are of course based on arbitrary assumptions. Particularly, on the assumption that the heat transfer coefficient between surface and catalyst is the same. This is hardly the case as this coefficient varies with the direction of flow, which may be at a right angle to the tubes in the case where the catalyst is arranged outside the tube.

It was found that the plate-oven required 71%, the catalyst outside-tube oven only 60% of the surface necessary in the catalyst in tube type for the same temperature difference (ΔT) throughout the catalyst. For varying ΔT, it appears that the specific cooling surface of the catalyst outside-tube oven depends largely on the tube diameter used in the design and the larger the ΔT, the more apparent is this advantage over the catalyst in tube type.

(13) New Reactor Design - General (c)(Cont'd.)

An example may illustrate this:

An oven containing the catalyst in 20 mm. tubes is operated to give a certain Δ T max. through the catalyst. The surface required is to be 100%. A plate oven, in order to give the same ΔT would require 71% of the cooling surface (actually 77%, since the surface of the tubes traversing the plates must also be counted). An equivalent "catalyst-outside-tube-oven" using 50 mm. tubes would require 75% of the surface but if 20 mm. tubes are used only 63% of the surface is required. If however the "basic" catalyst in tube oven were using 50 mm. tubes (indicating a higher Δ T is permissible), then the surface for a plate oven would still be 77%, but the catalyst outside tube oven employing 50 mm. tubes would need only 65%, and if 20 mm. tubes were used only 52%. Thus the advantage becomes more apparent as the heatload decreases.

The design of the furnace, finally proposed for the plant, may be seen from the attached drawing M 4949-1 (Ammoniakwerk Merseburg) and a patent application. The tube bundle consists of a multitude of bayonet type tubes closed on one end. The circulation could be forced, but it was considered preferable to install the oven at a slight incline (6°) to induce natural circulation. In order to find the minimum angle required for adequate circulation, tests were carried out to establish the velocities of air bubbles in water ascending in an inclined tube as function of the angle. This report is attached. It was determined that a 6° angle gave sufficient flow. The oven otherwise resembles closely the Lurgi reactor, in regards to catalyst arrangement, pressure and general layout. The catalyst is again enclosed in a sheet iron box.

One of the major advantages in the design of this furnace is the simple filling and removal of the catalyst since no plates are used. The commercial oven was to contain 6.8 m^3 of catalyst. The 18 mm. O.D. tubes were arranged in 28 mm. triangular spacing giving a total of 800 m^2 cooling surface per oven. Results obtained on this type reactor are described in the section of "Synol".

(d) Rheinpreussen Liquid Phase Reactor. (See reference I(b)/40 at end of this section).

(1) This oven has been mentioned above in connection with Rheinpreussen liquid phase development. See also the attached Rheinpreussen drwg. 45099.

(2) The reaction is carried out in liquid phase. The slurry is contained in a vertical pressure vessel 1500 mm. diameter and 9560 mm.

(13) New Reactor Design - General (d) (Cont'd.)

high, (when filled with 10 m^3 of catalyst slurry, the height of the liquid is 8060 mm.) Gas is introduced through the bottom by way of a multitude of ceramic discs, thimbles, or similar means. The heat of reaction is removed by a tube bundle consisting of a multitude of vertical bayonet tubes. The top head of the vessel can be removed to draw the bundle. The bundle has a total surface of only 350 m^2, which is considerably less than the required in gasphase operations.

(3) Horizontal oven. Another pilot plant reactor had been installed by Rheinpreussen but never put into operation. The furnace is similar to the one used by Lurgi consisting of a plate-tube bundle in a horizontal pressure vessel.

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(14) List of References.

The German documents listed below are available in the library of the Bureau of Ships in Washington, D.C.

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SYNTHESIS OF HYDROCARBONS AND CHEMICALS CO_2 AND H_2

SECTION I (c)

1. General Introduction.

The attempts to convert CO_2 with H_2 is not at all new, but it is of interest to note that the Germans obtained fair results using the identical catalyst as in the FT synthesis.

The work was carried out at the "Kaiser-Wilhelm Institut" in Muelheim (KWI). The catalyst used was described in detail in Section 18. It had been carbided at 1/10 atm. with CO at 325° C. Alkalized and non-alkalized catalyst was used.

Since the temperature of the synthesis must be rather high, the product is usually methane and a few g/m³ gasol. In fact the method was considered of interest mainly for the production of a standard city gas.

2. Operating Conditions.

Contraction data are given below based on feed gas: $CO_2:H_2=1:3$: V/H/V: 4 lit/hr/10 g Fe in catalyst.

	Non-Alkalized catalyst		1% K_2CO_3 in catalyst
Temperature	1 atm.	15 atm.	1 atm.
250° C	8	27	8
300° C	11	41	14
350° C	22	44	16
400° C	21	44	17
450° C	20	44	17

The influence of alkali is the same as in FT operation in that it raises the boiling range of the product. In this case alkali increases the liquid yield. Basis $CO_2:H_2$ = 1:3; 15 atm; 350° C, 2 lit/hr/10 g Fe.

% K_2CO_3	Contraction	g liquid/m³	g gasol/m³
0.0	30	3-5	1.5
1.0	40	16.0	11.0

2. Operating Conditions (Cont'd.)

Pressure increases the conversion. The following data show the contraction at different pressure:

Basis: Feed CO_2 : H_2 = 1:3; 350° C - 2 lit/hr/10 g Fe.

1% alkali in catalyst

Pressure	Contraction	g liquid/m^3	g gasol/m^3
15 atm.	40	16	11
30 atm.	47	24	15
60 atm.	58	39	23

Upon further increase in pressure the contraction began to decrease. Increased pressure also favors the synthesis of oxygenated compounds analogous to FT synthesis.

3. Reference.

The following German document is available in the library of the Bureau of Ships in Washington, D.C.

1. "Ueber die Umsetzung von CO_2 - H_2 Gemischen zu fluessigen und gasfoermigen Kohlenwasserstoffen" - by Dr. Pichler KWI.

THE SYNTHESIS OF HYDROCARBONS AND CHEMICALS FROM CO AND H_2

SECTION II

THE SYNOL PROCESS

SUMMARY

The attached report covers the development of the Synol process by I.G. Leuna. The process involves the direct synthesis of higher alcohols from CO and H_2 over a specially reduced iron catalyst at medium pressure.

The products were considered of outstanding quality being almost exclusively straight chain terminal alcohols. They were considered for use in the manufacture of lubricating esters and detergents.

The development was carried through laboratory and pilot plant stage and construction of a 30,000 ton/year plant at Leuan was considered.

Contents:

SECTION II

THE SYNOL PROCESS

1. General Introduction.

The synol process has been developed by I.G. Farben at Leuna under the direction of Dr. Herold. It is a new process for the production of oxygenated compounds, mainly alcohols. The hydrogenation of CO to form alcohols at high pressure is an established process (methanol synthesis and isobutanol synthesis). The synol process is one attempt to continue this series and produce higher boiling alcohols with the OH group in the terminal position, thereby differing from the α alkyl-alcohol of the oxo synthesis and the branched chain alcohols of the isobutyl synthesis.

The overall equation of the Synthesis may be written as follows:

$$28\ CO + 23\ H_2 \longrightarrow CH_3\ (CH_2)_8 - OH + C_8\ H_{16} + 11\ CO_2 + 5H_2\ O$$

This result, the direction of the synthesis towards the production of alcohols, was obtained by operating at intermediate pressures over iron catalysts, and at the lowest possible temperatures, 180° - 200° C. This in turn is made possible by a special reduction of the catalyst.

The development of the process was carried out mostly during the war. A series of patents, covering the essential features, were applied for in Germany only. Towards the end of the war it was decided to build a 30,000 ton/year plant at Leuna, but the project was still in the paper stage when the war ended.

The basic patent (see reference II/2, II/3 and II/4 at end of this section) applied for in September 1942 makes the following claim:

A process for the production of alcohols from CO and H_2 over Fe catalyst at elevated pressure, characterized by the operation at temperatures substantially lower than those required for the production of hydrocarbons over the same catalyst.

The patent further discloses the use of excess hydrogen in the preparation of the catalyst and the importance of keeping any trace of oxygen from the catalyst during and after reduction.

In another patent application, dated March 1943, the use of gas

1. General Introduction (Cont'd.)

recycle, with intermediate removal of the product, is disclosed as a means to increase the percentage of alcohols in the product to 70% and more. This is the same principle as the "Kreislauf" process for the increase of olefines.

2. Catalysts. (See also references II/26 to II/30 at end of this section).

(a) Preparation.

Fuzed as well as precipitated catalysts have been studied, but the ease in handling and reproduction and mechanical strength of the fuzed type led to the almost exclusive use of the latter. It is substantially identical with the Leuna ammonia catalyst. The catalyst may be prepared as follows:

Pure electrolytic iron or iron from carbonyl (99.9% minimum purity) was mixed with alumina to give a final mixture of 3.5% Al_2O_3 based on Fe, 0.15 to 0.5% K_2O are added and the iron is oxidized. If iron metal was the raw material, oxygen has to be used for the oxidation step. The exact final state of oxidation was not known, but the catalyst could be readily reproduced.

The melt is broken up into 1-2 mm. particles and reduced. The reduction requires hydrogen of high purity and a large excess of hydrogen is used. A temperature, however, of at least 420° had to be reached to obtain reduction.

Some X-ray studies had been made regarding the influence of the reduction temperature. It was found that at 400° C, Fe_3O_4 and Fe were present in the ratio of around 1:3. At 425° the ratio was nearer 1:4 while at 500° no more Fe_3O_4 could be found. By the same method it was further determined that the space velocity of the H_2 over the iron influenced the Fe_3O_4: Fe ratio. Thus: At 300 V/H/V, after 6 days, the ratio was still 0.75, but at 3000 V/H/V after 4 days it was 0.3

In a patent application, dated July 1941, the use of reduction with H_2 is disclosed, whereby the product of space velocity x time (days) must exceed 2000. This is apparently the lower limit.

(b) Reduction.

At the present time, the following conditions are used for the reduction:

2. Catalysts (Cont'd.)

Pure hydrogen (Sulphur - 0.10 gm/100 m^3) enters the system through a Pattenhausen grude tower to protect against break through of sulphur. The gas next passes a methanizer to remove traces of CO (the methanizer could however be omitted). The fresh H_2 is then added to the recycle, where it represents 3-5% of the total stream. The total hydrogen passes through silicagel drums, is dried and the dry hydrogen is blown through the preheater and the reduction vessel. The exit gas is cooled with water and NH_3 before being returned to the silicagel drier.

The reduction vessel (1400 mm. diameter) is filled with 500 liter fuzed Fe catalyst (0.5-1.0 mm.) The catalyst is retained on a bronze screen. Care is to be taken that no catalyst particles fall through the screen before reduction.

After thorough purging of the H2- circuit, the heater is fired and the temperature raised to 450° C within five hours. The dried H_2 is circulated at 2000 V/H/V.

The water content of this H_2 after drying is 0.5-2 gm/m^3. At the beginning of the reduction the H_2O content after the catalyst rises to a dew point of plus 4.0°C. Part of the water is condensed in the NH_3 cooler and the remainder is removed in the driers. A certain amount of NH_3 formed during the reduction is absorbed in the water.

The reduction is completed after 50 hours. The system is cooled and CO_2 admitted slowly to avoid overheating from the absorption of CO_2 on the catalyst. This CO_2 used for blanketing must be dried over silicagel and must be free of sulphur.

In handling, utmost care must be taken to prevent all oxygen from coming in contact with the catalyst. Even the slightest poisoning of the reduced iron with air or oxygen requires a higher initial synthesis temperature (less alcohols) and shortens the catalyst life. The apparent density of the finished catalyst varies from 1.8 to 2.2 according to particle size.

The life of the catalyst is around 9 months. For the design of a plant, which was to make catalyst for a 10,000 ton/year synolplant, an average life of only 4 months had been assumed. It is noteworthy that additions of several tenths of 1% of arsenic to the catalyst results in a substantial increase of esters (25% in the 200°- 300° C fraction). In the synthesis the catalyst immediately forms Fe2 C of hexagonal crystal structure and above temperature of 290° C this carbide is converted to an inactive form.

2. Catalysts (Cont'd.)

Particle size: It is of interest to note that the change in catalyst particle size had considerable effect on the results. Towards the end, I.G. used sizes between 0.5 and 1.0 mm. This led to increased output from the unit catalyst volume. It was concluded that the inside of the particles did not participate in catalyzing the reaction.

The drop in catalyst size from 1 - 2 mm. to 0.5 - 1 mm. made it possible to lower the temperature from 198° to 191° C. This in turn increased the ratio of $H_2O : CO_2$ in the reaction products, since the shift decreases at lower temperature.

Synthesis in "fluid bed" reactors and fluid bed reduction tests had been scheduled but were never started.

3. Synthesis - Operating Conditions. (See ref. II/1 to II/13 at end of this section).

(a) CO_2 Formation.

The CO and H_2 are consumed in the synol synthesis in the ratio of 1.1:1.0 ($CO:H_2$) but regular watergas ($CO:H_2$ = 1.0:1.1) may be used for the synthesis. The catalyst is susceptible to sulphur poisoning and requires a feed gas as equally pure as the FT plants. A maximum of 25% inerts in the gas was acceptable.

It was stated that the synthesis should be carried out at the lowest temperature possible.

It was found practical to use the formation of CO_2 as controlling variable for the maximum production of alcohols. The less the conversion proceeds in one stage, the less CO_2 formed and the more alcohols recovered. 10% is considered the maximum value for the volume % of CO_2 in the exit gas from the synthesis. The CO_2 may be scrubbed out before entering the next stage or returning the gas to the reactor (recycle).

(b) Temperature.

Over a given catalyst and at a definite pressure and CO content of the feed, the temperature in the reactor is the means for control of the conversion one wishes to obtain. This temperature is between 190 - 195° C in the first stage and may exceed 210° C in the following stages depending on the inert content of the gas, particularly the CO_2 content. CO_2 in

3. Synthesis - Operating Condition (b)(Cont'd.)

quantities of 5 - 6% has a poisoning effect in that it requires a higher synthesis temperature and thus lowers the alcohol yield.

Towards the end of the war the German government lost interst in the synol development and insisted on directing the research toward production of fuels. I.G. then planned to continue with the installation of the synol plant, but operate under conditions which would give little alcohol and mostly olefines ("Benzinfahrweise"). This could be done very simply by raising the temperature of the synthesis. The operation at 260 - 300°C over the same catalyst produced a gasoline of 40-60% olefines with 65-75 octane number (res.). This operation was admittedly a means to continue work on the project and is not considered an improvement over the synol operation.

In order to illustrate the difference in the two methods, the following data are listed below giving results from two types of operation:

Both columns refer to the identical fuzed iron catalyst:

Type of Operation	Synol	Gasoline
Pressure	25 atm.	25 atm. maximum
Temperature	190-225°	210-245°
Feed Gas	Watergas	S free
Yield gm/m³ $CO+H_2$	150 gm liquid	140 gm liquid
	50 gm gasol	14 gm gasol
Stages	4	3
Space velocity V/H/V	150	250
Specific output tons/m³ catalyst/day	0.60	0.92
Catalyst life	9 months	6 months
Product Distribution:		
Gasoline - 200° C	44-60%	40-70%
"Diesel" 200-300° C	18-15%	30-15%
Gasoil 300-400° C	15-10%	30-15%
400° C	23-15%	-

The alcohol and olefine content of the various fractions from Synol are as follows:

Fraction	Alcohol	Olefine	Paraffin and Rest
200° C	40-50%	45-30%	5-30%
200-300° C	56%	20-30%	14-24%
300-400° C	50-60%	15-25%	15-35%
400° C	10-30%	45-30%	25-60%

3. Synthesis - Operating Condition (b)(Cont'd.)

Note: Between 200-400° the "Rest" varies from 3 - 8%.

In general the increase in temperature lowers the alcohol and increases the olefine yield. As the catalyst ages, it slowly loses its activity and requires increasingly higher temperature. Thus the alcohol yield decreases over the life of the catalyst.

The same general rules, applicable in FT operation apply equally in synol: more alkali in the catalyst, lower temperatures, lower space velocity (within limits) give higher boiling products. There were however, indications that the desirable middle fraction could be increased individually by using precipitated instead of fuzed catalyst of identical composition. The reasons for this were not recognized.

(c) Pressure.

The preferred pressure range for the synol synthesis is 18 - 30 atm. (25 at optimum). At higher pressure the Fe-carbonyl formation is substantial. At the same time it becomes more difficult to remove the heat of reaction and this in turn leads to carbon deposition on the catalyst. The alcohol/olefine ratio is little affected by pressure.

(d) Recycle.

The "Kreislauf" operation described in Section I(a) of this report may be used equally well in synol operation. It is simply necessary to remove substantially all water from the reaction product before returning the gas to the oven. This drying tends to suppress the CO_2 formation sufficiently to obtain 90 - 93% conversion (on a gas containing 6% inerts) without intermediate scrubbing of the CO_2. The removal of CO_2 particularly by way of the alkalized-type processes is not easy in this case due to the fatty acids formed in the synthesis.

It was also found that the life of the catalyst was dependent on the partial pressure of the water in the reactor. In a "Kreislauf" run when the water was removed from the reaction products before recycling, and using 2500 V/H/V total gas load, the catalyst ran 7 months without losing its activity. This compares in the once through (3-stage) operation with a maximum of 3 - 4 months catalyst life.

Another beneficiary effect of the "Kreislauf" is of course the immediate removal of the synthesis products from the reactor. Thus any

3. Synthesis - Operating Condition (d)(Cont'd.)

secondary dehydration or hydrogenation is suppressed. The higher alcohols in the C14 - C17 range are particularly affected by this operation. Due to the increased gas volume, these products are swept out of the reactor as vapors. In the once through operation they condense on and are decomposed by long contact with the catalyst.

Using recycle space velocities of 2000-3000 V/H/V (based on total feed) allows 90-94% conversion in two stages only (while 4 are required in the once through operation). Under these conditions 1 mol. CO_2 is then formed from 12 mol. feed gas.

Some operating figures may illustrate the Kreislauf operation:

The data are based on a fresh feed gas of the following composition:

CO plus H_2	86.0%
CO_2	5.5%
CH_4	5.0%
N_2	3.5%

Change of recycle gas composition with conversion (1 stage only)

% CO plus H_2 converted	Kreislauf composition			
	CO plus H_2	CO_2	CH_4	N_2
90%	25.7	44	19.6	10.6
85%	35	38	17.5	9.5
80%	42	33.5	15.8	8.7
65%	62.5	17.3	12.9	7.3

These figures are all based on the same catalyst volume. Thus to obtain higher conversion at lower CO - H_2 content the synthesis temperature must be raised; this in turn increases the CO_2 production (the conversion to CH_4 was assumed as 8% in all cases).

Operation in liquid phase was not considered applicable for synol because long contact on the catalyst is characteristic for this technique. However, the use of "Kreislauf" may make liquid phase operation feasible. I.G. had proposed to study this process but the end of the war prevented further work).

4. Equipment.

The inclined synol reactor has been described in detail in the preceding Section I(b). It is in principle a reactor using a flat catalyst

4. Equipment (Cont'd.)

bed. The cooling tubes were embedded in the catalyst and were designed as bayonet tubes with one end closed. This arrangement was chosen to facilitate filling and removal of the fine grained catalyst.

For a further development the Germans had designed a twin oven consisting of a common centerpiece which carried 2 inclined cooling coils within the catalyst. Each bed was to contain 6 m^3 of catalyst.

There had been several different pilot plant ovens used in the laboratories including 2 vertical tube-reactors with the catalyst inside the tubes. (Tube diameter 15 and 20 mm.) At the same time a horizontal plate reactor (inside a pressure drum) was also installed. This unit is practically identical with the Lurgi design. Only one short run was made with this oven.

In order to protect the catalyst in case of a failure in the cooling system hydrogen was admitted and all CO purged from the catalyst as fast as possible.

The catalyst apparently forms a solid mass at the end of the run and must be drilled out of the tubes (80 working hours to empty 1300- 15 mm. tubes). Before the catalyst can be removed it is first extracted with an intermediate fraction of the product (150 - 240° C) by passing the liquid through the tubes for 1/2 hour. It is then dried and deactivated with N_2.

The unloading procedure in the case of the plate reactor was still more complicated.

The new design (inclined tube handle) had not been tested in any large scale pilot unit, but the I.G. engineers had great hopes that it would solve all problems. All other equipment used in the pilot plant such as blowers, CO_2 washers, coolers, charcoal adsorbers were conventional.

5. Products from Synol Operation. (see reference II/14 to II/18 at end of this section).

(a) Alcohols.

It has been stated that the main objective of the synol process was the production of straight chain terminal alcohols of boiling range as high as C_{20}. Thus a new class of chemicals had been developed from a

5. Products from Synol Operation (a)(Cont'd.)

laboratory curiosity to a commercial product. It has already been described how this objective could be reached, but the inventors themselves could not give an exact answer why it was possible to do it by way of the process described.

One German expert offered the explanation that alcohols are the primary products when the synthesis is carried out at low temperatures. They are dehydrated to olefines in a second step. This assumption may find some basis in the fact that the sum total of alcohol plus olefine in synol operation is fairly constant over a wide temperature range.

The products leaving the reactor are recovered in an oil and water phase, the water containing up to 25% organic compounds. These compounds include low boiling alcohols, ketenes, aldehydes, acids and esters, and some salts of short-chained fatty acids. The oil phase contains enough high boiling products to solidify at room temperature. The methods used to separate the products are given in a later section.

The constitution of the products has been studied in great detail. The alcohols, up to C9 are practically straight chain primary alcohols. No secondary alcohols can be found. The same is substantially true of the higher alcohols (methanol and ethyl alcohol are produced only in traces).

(b) Olefines.

The olefines are mostly α-olefines. A C_{12} olefine was analyzed and found to have 60% of the double bond in α-position, while the rest was distributed with decreasing percentage toward the middle of the molecule. It was concluded that primarily all olefines are terminal, but due to isomerization the double bond is moved towards the middle of the molecule. Iron carbonyl is believed to catalyze this shift. A similar effect was observed in the oxo-synthesis where the presence of cobaltcarbonyl causes a shift of the double bond.

The sum of alcohols plus olefines in the product is between 70 - 80%, the alcohol ranging around 60% and over.

(c) Esters.

Esters are always present in certain fractions. That arsenic in the catalyst increases ester production up to 25% has already been stated. The ester content generally increases with the boiling range. Esters make

5. Products from Synol Operation (c)(Cont'd.)

up as much as 10% in the C_{10} alcohol range and increase to 20% in the C_{18} range.

The formation of the ester (and acid) has been explained by the direct reaction of CH_2 radicals with CO and water. In the preparation of fatty acids from alcohols and CO, the following chain of reactions is assumed to take place:

(1) Decomposition of the alcohol to free radical and water

$$CH_3\ OH \longrightarrow CH_2 = H_2O$$

(2) Reaction of radical and CO to form ketene

$$CH_2 = + CO \longrightarrow H_2\ C = CO$$

(3) Ketene may react with water or excess alcohol to form the corresponding acid or ester:

(a) $H_2C = CO + H_2O \longrightarrow CH_3\ C\ O\ O\ H$

(b) $H_2C = CO + CH_3OH \longrightarrow CH_3\ COOH_3$

The free radical is of course extremely short lived and present in only small concentration. It is therefore necessary to operate with high CO concentration to have the necessary acceptor ready to react with CH_2 the moment it forms. This explains the high CO and low alcohol concentration required for this process. The theory may be applied to FT or synol syntheses and offers a good explanation for the high acid and ester yield. The presence of CH_2 radicals in the hydrogenation of CO is generally acknowledged and with CO and H_2O (or alcohol) also present, the synthesis to acid and ester could follow the chain of reactions described above.

(d) Aldehydes and Ketones.

Aldehydes and ketones are both found in the product. The lower aldehydes can be extracted with bisulfite solution. The ketones are more stable and give no trouble. During the separation of the alcohols with boric acid they remain in the neutral oil. The lower ketones (acetone) are found mostly in the aqueous phase. There are some other classes of oxygenated compounds found in the primary product such as esters and unsaturated ethers, but they rarely make up more than 1% of the total. The products recovered and isolated so far are mostly the alcohols from C_1 to C_{22}.

5. Products from Synol Operation (d)(Cont'd.)

The products obtained from synol operation according to "Benzin-Fahrweise" resemble those contained in FT synthesis over Fe catalyst.

The gasolines from synol must be refined before they can be used as motor fuel. They are unstable and corrosive and do not have a sufficiently high octane number (see reference II/17 at the end of this section).

A raw gasoline had the following properties:

Distillation	IBP	35° C
	50%	108° C
	90%	148° C
	EP	200° C
Gum (after 7 days)		202 mg.
Cu strip		colors gasoline blue
OH number		191
Octane No. (res.)		54.0

The gasoline was refined over Fullers earth at 300° C., using 0.5 - 1 volume liqu./hr/volume Fuller's earth. The resulting product was as follows:

Distillation	1 BP	34° C
	50%	90° C
	90%	180° C
	EP	198° C
Gum (after two days)		0.5 mg.
Cu strip		Negative
OH number		6.5
Octane No. (res.)		72.5

The treatment consists essentially in dehydration of the alcohols to olefines and condensation of the aldehydes to high boiling polymers which are fractionated out.

The losses depend of course on the alcohol content and thus on the temperature of the synol operation itself. The increase in ON is substantial, but I.G. had still further considered the use of olefine isomerization to shift the terminal double bond towards the middle of the molecule as an additional means to improve the knockrating.

The diesel oils obtained in this operation do not compare with those from cobalt catalyst FT plants. 62 Cetane number was given as an average value.

6. Uses for Synol Products.

This problem was of great interest since some of the products are a new commodity on the chemical market. Of greatest importance appear the alcohols. The C7 - C11 range may be esterified with acids of equal chain length (produced from the same alcohols) and used as plasticizers. The C9 - C14 fraction can be used for esterification with adipic acid to produce outstanding lubricants. This is an important use. The lower alcohols $C_3 - C_8$ may also be used for esterification to yield lacquer solvents. The synol alcohols are preferred on account of their straight chain character.

However, the most important application (in Germany) would have been the use of the higher alcohols in the detergent field. Due to their straight chain structure synol alcohols resemble the natural fatty alcohols. From them they differ only by way of their content of even and uneven numbered carbon atoms. The uses for the corresponding olefines are well known, with polymerization to synthetic lube oil in first place and sulphonation for the production of emulsifiers and detergents as an alternative. This entire field is presently in a state of development.

7. Separation of Products.

The separation of the various products has been the subject of considerable work by I.G.

(a) Pretreatment.

Before the alcohols, olefines and the neutral oil can be separated, it is necessary to take certain steps regarding the undesirable by-products As such, are classified the acids and their reaction product with alcohols, the esters. Other undesirable compounds are the aldehydes and ketones which appear in only small quantities.

The acids must be neutralized with alkali to prevent further alcohol losses to esterification. A simple caustic wash is sufficient for this purpose. If it is also desired to de-esterify the product, the caustic wash may at first be omitted.

The esters are preferably saponified with strong alkali at 130° C. A 30 minutes treatment with good agitation is sufficient. The alcohols are thereby set free and the acid neutralized by the alkali. At the same time the reactive aldehydes are condensed to form heavy polymers and thus wind up in the high boiling fraction (see on the next page).

7. Separation of Products (a)(Cont'd.)

If the esters are not removed, they appear in the following fractionation according to their boiling range and thus induce alcohols and acids into these fraction where they do not belong.

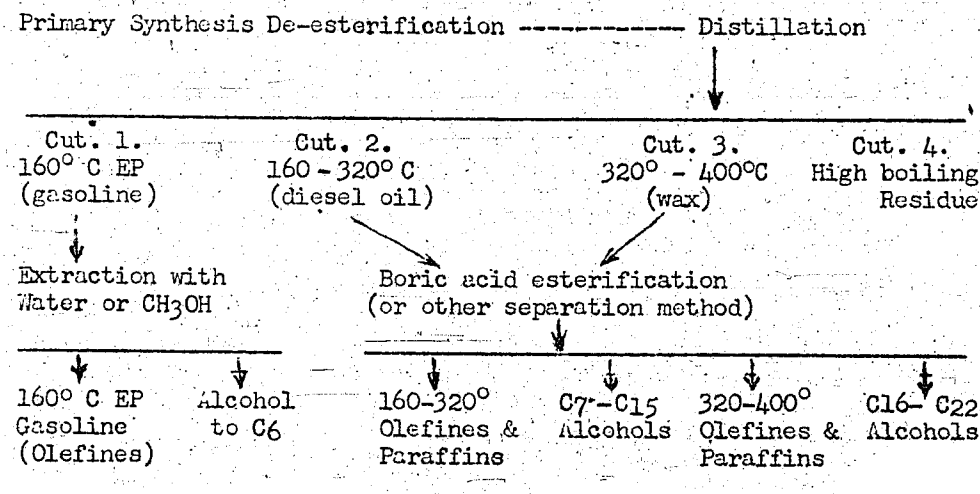
(b) Fractionation. (See reference II/21 at end of this section).

A sharp fractionation of the raw product is apparently essential for the exact separation into alcohols and hydrocarbons. This is particularly the case when boric acid-esterification is used as a means of separation.

The lower alcohols (to C_3) are practically completely dissolved in the aqueous phase of the product. The C_4 to C_6 alcohols may be washed out with water or possible methanol-water solution. This water wash is automatically carried out when the product is first de-esterified since the alkali must be washed out with water.

The higher alcohols may be separated and prepared in 95 - 97% purity, provided the original feed is fractionated sharply. Several methods were studied by the Germans.

A simplified flowchart of a synol process may look as follows:



7. Separation of Products (Cont'd.)

(c) Boric Process. (See reference II/22 at end of this section).

Boric acid esters are used for the separation of higher synol alcohols from the accompanying olefines and neutral oil. It is essential that the feed to the esterification unit be fractionated as sharp as possible. 50° C boiling range appears to be satisfactory for each cut.

One of the difficulties which require further work is the distillation of the neutral oil from the boric acid ester. The mixture must be thoroughly agitated. At the same time a temperature in excess of 250°C must be avoided in any step of the process.

The highest alcohol produced to date by this method is C_{22} H45OH. Higher alcohols cannot be separated from the oil without decomposition.

The principle of the process is based on the fact that

(a) The alcohols esterify readily with boric acid at elevated temperature.

(b) The esters are considerably higher boiling than the alcohols (and accompanying compounds).

(c) The esters are easily hydrolyzed with water and the alcohols recovered.

In the process of this type the boric acid used for esterification must be substantially pure B_2O_3. But at the same time only a dilute solution of B_2O_3 is obtained in hydrolyzing the ester. This operation is expensive since large quantitites of solution must be concentrated.

It was found however, that a saturated aqueous solution of boric acid could be used in the hydrolysis step. This solution could be separated from the free alcohol by settling, and upon cooling, the additional free acid would precipitate from the solution. The acid crystals could be recovered by filtration and used immediately for further esterification. The process is applicable to all types of alcohols and in particular for the oxo process.

The esterification yields a certain quantity of water which must be removed. This is done by extractive distillation with benzine. The esterification requires elevated temperature, and thus the water and benzene are simply carried overhead as they form.

7. Separation of Products (c)(Cont'd.)

Following the removal of the water, the neutral oil is distilled to leave pure ester in the kettle of the column. The ester is then hydrolyzed with hot aqueous boric acid solution.

Below find operating data for one example:

The raw material from the synthesis has the following composition:

Alcohols	50% vol.
Olefines	40% "
Paraffins	9% "
Acid, Ketones etc.	1% "
	100% "

This mixture was fractionated to give the following cuts:

(1)	0-100° C	30% vol.
(2)	100-200° C	20% "
(3)	200-300° C	16% "
(4)	300-400° C	17% "
(5)	400° C +	17% "
		100% "

The object was to recover the alcohols boiling between 200° and 400° C. For this purpose fraction 3 and 4 were treated separately.

Treatment of fraction 4:

Feed: 100 kg. of fraction containing 72% wt. alcohol.
6.6 kg. boric acid.
575 kg. benzene

The mixture is agitated and heated to 90° C for 2 hours.

575 kg. benzene
4.8 kg. water } distilled overhead

Distillation is then continued under vacuum.

The neutral hydrocarbons distill overhead. A total of 28 kg. is recovered in the receiver.

The kettle product, i.e., the boric acid ester after is transferred to the saponifier, where it is treated at 95° C for 30 minutes with 55.5 kg. of a 2.6% aqueous boric acid solution. The free acid solution is then allowed to settle at 95° C and is withdrawn. The solution now containing

7. Separation of Products (c)(Cont'd.)

10.9% wt. (i.e., 38.8% saturation at 95° C) is next cooled to 2° C. The excess boric acid crystallizes and is centrifuged. 5.2 kg. boric acid are thus recovered. The filtrate, 50.5 kg., is returned to the system.

The free alcohols, 72 kg., are also withdrawn from the saponifier. 1.5 kg. boric acid still remain in solution. For its removal the alcohols are washed with 56.2 kg. water. The alcohol passes 3 counter current wash stages.

(d) Separation by Silicagel Adsorption. (see ref. II/25 at end of this section).

This method was considered by the Germans at one time for the separation of synol alcohols and deserves to be mentioned here.

The method is based on the difference between the heat of adsorption between alcohols and hydrocarbons.

	Heat of Adsorption		
methanol	15.0	Cal/gm	Silicagel
ethanol	14.8	"	"
n+butanol	13.0	"	"
n+octanol	12.0	"	"
n+decylalcohol	12.7	"	"
n+hexane	5.3	"	"
n+dodecane	6.1	"	"
water	16.1	"	"

The mixture is contacted with the dry gel and then washed with a volatile low boiling hydrocarbon solvent (petrol ether). The hydrocarbons are thereby removed. The alcohols remain adsorbed and may then be removed by such polar solvents as lower boiling alcohols or ketones and ethers. The gel is finally regenerated.

The gel may be loaded according to its quality, the particle size (1-2 mm) and the alcohol boiling range. For 170-180° alcohols, 15 g/100 g gel may be reached.

The adsorption must be carried out at room temperature or even below. The alcohol should be desorbed as soon as possible. The regeneration of the gel may be carried out with hot gases (N_2, CO_2) at 150° C and 1:1000 V/H/V.

7. Separation of Products (c)(Cont'd.)

(e) Separation of Azeotropic Distillation. (see ref. II/24 at end of this section).

Glycols are known to form azeotrope mixtures with many classes of organic compounds. In the case of synol products it was found that glycols may be used for separation because:

(1) Their azeotropes with hydrocarbons boil considerably below their azeotropes with equally high boiling alcohols.

(2) The azeotrope with hydrocarbons contains considerably more hydrocarbons than one with the alcohols.

(3) The glycols and the hydrocarbons in the overhead separate into two phases in most cases.

(4) The alcohols which are carried over the top remain dissolved in the glycol phase and may thus be easily returned to the column.

Particularly suited are of course those glycols which form azeotropes with hydrocarbons only and not with the alcohols. Butanediol 1-3 and hexane-diol 1-6 fall in this category.

Another particular advantage of these compounds is their high efficiency, i.e., the low volume ratio between the azeotropic carrier and the overhead component. This ratio may further be lowered by operation under vacuum. The following figures may serve as an example:

Using butanediol 1-3 on a 230 - 245° fraction the ratio of glycol to hydrocarbon is 2:1 at 1 atm., but only 1:1 at 20 mm. Hg.

In selecting the third component it is desirable to have the initial boiling point of the mixture 10-20° C above the boiling point of the carrier The other oxygenated compounds such as ketones and esters are usually distilled overhead with the hydrocarbon.

It is possible first to enrich the mixtures of synol products in alcohol content by selective extraction with methanol. Thus 80% alcohols may be obtained in the mixture. 100 pts. of such a mixture (230 - 270° C) are distilled with 10 parts butanediol 1-3 at 20 mm. Hg. to give an alcohol concentration in the kettle as high as 98%.

The process is generally limited to alcohols from C8 on up.

7. Separation of Products (Cont'd.)

(f) Separation by Extraction with Aqueous Methanol. (See ref. II/23 at the end of this section).

The process is based on the higher solubility of the alcohols in the methanol solution. The necessary quantities to reach an alcohol concentration of 97% are given below.

Synol Fraction	Alcohol Content	CH_3OH Conc'n used	Vol. CH_3OH Solution for 1 vol. Synol	% Alcohol in the neutral oil.	% Non-alcohol in the Alcohol
120-170° C	56	68	2	0.1	3.0
170-220° C	48	76	3	0.3	3.0
220-270° C	40	81	6	0.6	3.5
270-320° C	29	85	10	1.0	3.5

For practical purposes the extraction method is limited to C_{12} alcohols maximum.

The methanol is separated from the extract by distillation. Upon removal of the CH_3OH, the higher alcohols and the water separate into two phases and the water is withdrawn.

The methanol extraction or enrichment may be of interest in combination with the use of glycol to obtain final alcohol concentration (see above).

(g) High Boiling Products.

It was pointed out that prior to separating the alcohols from the neutral oil, the raw synol product had to be fractionated. The fraction boiling above 400° C was not considered in the process. Alcohols above C_{22} cannot be prepared by the boric acid method as the neutral oils cannot be removed from the ester by distillation.

The high boiling product is dark brown, probably due to Fe which is contained in quantities up to 0.1% (due to ironcarbonyl). The product may be used as such for certain industrial purposes. It can be treated with Fullers earth to give slightly yellow waxes. Pour points are usually varied from 70 to 105° C. The high ester content of these products makes them more ductile than FT wax. If necessary they may be hydrogenated to give high melting point waxes of the FT type.

8. Conclusion.

The synol process may be considered the most important development in the field of $CO-H_2$ synthesis carried out in Germany during the war. It is a means to synthesize in one operation a valuable chemical, such as high boiling alcohols.

The process appears to be entirely practical and requires no extreme operating conditions or expensive catalysts. It is the first achievement in the general trend to direct Fischer-Tropsch type synthesis away from fuels and hydrocarbons and towards especially defined compounds. It seems likely that the synol process, with certain variations could be changed to produce oxygenated compounds, such as esters and acids.

9. List of References.

There are appended to this Section II the following German documents:

1. "K-Synthese aus CO and H_2 Stand am 1. August 1942" - by Wintzer, Reisinger, Breywisch.
2. Verfahren zur Herstellung von Sauerstoffhaltigen Verbindungen - Patent Dept. Leuna, 23 September 1942.
3. Herstellung von sauerstoffhaltigen Verbindungen - I.G. Farben patent application, 15 October 1943.
4. Verfahren zur Herstellung von O2-haltigen Verbindungen - Kreislauf Verfahren - 8 March 1943.
5. Verfahren zure katalystischen Reduktion von CO und H_2 - I.G. patent application, 23 June 1943.
6. Synolsynthese - by Breywsich April 1943 - Referat Merseburg #10
7. Die Synolsynthese - by Reisinger, February 1943 - Austausch der THK.
8. Bericht #472 by Breywisch, 10 October 1944 - Erfahrungen mit den halbtechnischen Synolanlagen Me 458.
9. Bericht #283 by Reisinger, 2 May 1941 - Bericht ueber Synol Synthese.
10. Bericht #326 by Wenzel : 10 April 1942 - Stand des Synolproblems.
11. Unterlagen fuer den Bau einer 10,000 jato Synolanlage - by Wenzel, 24 December 1940.
12. Stufenfahrweise der Synolanlage Leuna - by Gemassmer - 21 September 1943.
13. Erlaeuterungen zum Schema BSK 66 - 17 June 1943 incl. one drwg. BSK 66.
14. One drwg. M:4342-1 24 July 1941 - Schema fuer die Destillation der Synolanlage Leuna.
15. One drwg. M-4375-1 - Schema fuer die Syntheseanlage d. Synolanlage Leuna.

9. List of References (Cont'd.)

16. Four diagrams re: product distribution from synol process: by Wengel and Reisinger, 20 March 1941. 0/1227/3 - SK/1606/a - SK/1606/b - SK/1606/c
17. Pruefungsergebnisse von Synolprodukt als Kraftstoff - by Hilberath, 25 May 1945.
18. Gesetzmaessigkeit bei d. Dehydratisierung hoeherer Alkohole - by Asinger, 9 April 1943.
19. Zusaetzliche Esteroel-Alkohole - 9 July 1942 by Pohl.
20. Aktennotiz re: Nachbehandlung von Synolprodukt fuer Motortreibstoffe, 9 January 1942.
21. One drwg. Fliess-und Mengenschema fuer Verarbeitung der Synolprodukte, M-9802-2
22. Verfahren zur Abtrennung von Alkoholen aus nichtwaesserigen Fluessigkeiten. 7 April 1941.
23. Abtrennung aliph. Alkohole d. Estraktion mit waesserigen Methanol by Menzel, 22 November 1944.
24. Verfahren zum Entfernen von Nicht-Alkoholen aus Alkoholgemischen durch Azeotrope Destillation - 15 February 1945.
25. Abtrennung von Alkoholen aus Gemischen mit Kohlenwasserstoffen - by Geiseler, April 1943.
26. Verfahren zur Reducktion eisenhaltiger Katilisatoren - patent application, 7 July 1941.
27. Roentgenfotografische Analyse von Kontakten - 2 July 1941.
28. One drwg. M-6459-4 - Schema der Kontaktreduktion.
29. Reduktion von Eisenschmelzkontakt - 15 July 1943.
30. Erweiterung und Verbesserung der Reduktion von Kontakt fuer Synol - 6 March 1943.
31. Mechanismus der Bildung von Fettsaeure aus CO und Alkohol - by Dr. O. Fuchs - 4 May 1936.

SYNTHESIS OF HYDROCARBONS AND CHEMICALS FROM CO AND H_2

SECTION III

SYNTHESIS OF HIGH MELTING POINT WAXES

SUMMARY

The attached report covers laboratory work carried out by Kaiser-Wilhelm-Institut on the synthesis of high boiling waxes over Ruthenium catalyst. The results have been published in 1940 - 1941. They are mainly of theoretical interest.

Content.

THE SYNTHESIS OF HIGH MELTING POINT WAXES

1. General Introduction.

The use of Ruthenium as a catalyst for the production of high M.P. wax from CO and H_2 was published in 1941 in "Breunnstoff Chemie". 19.22 . P.226, the monthly magazine published by Kaiser Wilhelm Institut at Muehlheim. Copies of this paper are available in the United States for ready reference. The information obtained on the subject is briefly given in this report.

The process is mostly of theoretical interest and was not carried out beyond the laboratory stage.

A patent application was filed on May 1938 disclosing the use of Ruthenium (and/or catalysts containing Ru) at temperatures from 150 to 280° C and pressures above 30 atm. for the production of solid aliphatic hydrocarbons from CO and H_2.

2. Catalyst.

The catalyst is prepared by melting Ruthenium with KNO_3 and KOH to give potassium ruthenate which is dissolved in water and boiled under addition of methylalcohol. RuO_2 is precipitated, filtered, washed, and dried. The oxide is reduced with synthesis gas ($CO:H_2 = 1:2$) at 150° C and atmospheric pressure.

The catalyst may however be prepared by different methods. The essential requirement is that Ruthenium be present in as great dispersion as possible. Carriers, such as Kieselguhr may be used, but they have apparently no effect on the synthesis.

3. Operating Conditions.

The yield in hard wax increases with pressure and decreases with temperature. Optimum conditions seem to be 195° C at 150 atm. pressure.

Space velocities from 1-2 liter gas/hr/gm Ru are used. The yields given by KWI are 150-160 g/m^3 ideal feed gas.

The catalyst is quite susceptible to poisoning by sulphur, but with a pure feed gas, its life is exceedingly long. A two year run was made with one charge without any catalyst regeneration.

3. Operating Conditions (Cont'd.)

It should be noted that I.G. Leuna tried to duplicate the results without success. They obtained a brown product containing only 40% hard wax. The catalyst furthermore lost its activity within a few days. It appears that sulphur containing gas may have been used.

4. The Products.

The product is a wide mixture of high boiling waxes. The paraffins are mostly exclusively straight chain hydrocarbons with only a small percent of tertiary carbon atoms.

The waxes were separated by known methods such as extraction at increasing temperatures and different solvents.

Individual waxes with molecular weights of 10,000 were found having a melting point of around 140° C. This seems to be the maximum melting point. Increased mol. weight does not further influence the melting point.

5. Reference.

The following German document is available at the library of the Bureau of Ships in Washington, D.C.

1. Patent application by KWI dated 7 May 1938.
"Verfahren zur Herstellung von festen aliphatischen Kohlenwasserstoffen".

RESTRICTED

THE SYNTHESIS OF HYDROCARBONS AND CHEMICALS FROM CO AND H_2

SECTION IV

SUMMARY

The attached report covers the development of the isosynthesis by "Kaiser Wilhelm Institut" of Muelheim. The process includes the synthesis of low boiling isoparaffins (particularly isobutane) from CO and H_2 over thoria catalyst at pressures between 200 and 1000 atmospheres.

All work connected with this process was carried out in laboratory scale only.

ISOSYNTHESIS

Content.

ISOSYNTHESIS

1. General Introduction. (See also ref. IV/1 and IV/2 at the end of this section)

The synthesis of low boiling isoparaffins was discovered in the laboratories of the Kaiser Wilhelm Institut at Muelheim. The discovery was made accidentally, when various oxides were studied for their use as catalysts in the synthesis of aromatics. It was observed that thorium oxide gave a high percentage of iso paraffins.

The process is a variation of the methanol or rather isobutyl synthesis. It operates at temperatures above those used in methanol synthesis, although CH_3OH is believed to be an intermediate product. The temperature range for the synthesis is limited on the one hand by the decomposition of CO (carbon deposit) at roughly 550° C. This limit is constant for all pressures. The lower temperature limit on the other hand is a function of the operating pressure. At 1000 atmospheres the isosynthesis may be carried out at 400° C. At 100 atmospheres a minimum of 450° C is required. More detailed information is presented in the following paragraphs.

2. Chemistry of Synthesis.

The Kinetics of the Synthesis is assumed to be as follows:

(1) Formation of Methanol from CO and H_2.

(2) Dehydration of alcohol and immediate reaction with additional CO and H_2 to isobutylene and higher isoparaffins.

(3) Polymerization of isobutylene possibly followed by hydrogenation of alkylate, or formation of dimethylether from methanol through addition of CO and H_2.

At very high pressure the reaction proceeds in the following direction

$$CH_3OH + CO + 2H_2 \text{ -------- } CH_3OCH_3 + H_2O$$

The dehydration of the methanol is an important step and operation at temperatures above those favoring methanol formation are specified.

Isobutane is one of the main products but the reaction is necessarily not as clear cut as presented above. It is also noteworthy that a small fraction of naphthenes and aromatics is usually found in the products.

2. Chemistry of the Synthesis.(Cont'd.)

The theory is in good agreement with the fact that the addition of dehydration catalyst to the thorium oxide has a beneficiary effect on the yield.

3. The Catalysts.

It was pointed out that the catalyst used initially was pure ThO_2. Some 10% alcohols (mostly water soluble) are obtained with thorium alone. The addition of aluminum (or other dehydrating catalysts) yields a product almost free of oxygenated compounds.

(a) Thorium Catalyst.

Basic thorium carbonate is precipated with soda from thorium nitrate solution and the precipitate washed free of alkali. Even small traces of alkali lower the catalyst activity and require higher synthesis temperatures. The filtered thorium carbonate is dried at 110° C, pelleted, and finally treated at 300 - 400° C with air passing through for 1 to 2 hours (no reduction is necessary).

The thoria catalysts are outstanding in their insensitivity to suphur poisoning. Treatment with H_2S or CS_2 does not effect the activity; even the use of $(NH_4)_2S$ for precipitation of the thoria gives normal conversion.

The long life of this catalyst is remarkable. It may be used several months without sign of aging. Even in case of carbon deposits and the resulting increase in pressure drop through the bed, the original activity can be restored by passing air over the catalyst at synthesis temperature.

The results obtained on pure thoria catalyst are given in the section on operation.

(b) Mixed Catalyst.

The high price of thoria and possibly its lack in Germany led to attempts to use substitutes and it was found that most dehydrating catalysts such as oxides of aluminum, sirconium, tungsten, or rare earths can be used provided that sufficiently high pressures are applied. On 2 October 1943, a patent application was filed disclosing the use of these substances either alone or in a mixture of thoria.

2. Chemistry of the Synthesis (Cont'd.)

It is claimed that these dehydrating substances direct the synthesis towards oxygenated compounds below a certain temperature. Beyond this limit, however, isoparaffins are the main product. In addition to the dehydrating components it was found that substances which catalyze the formation of CH_3OH at temperatures below those of the isosynthesis are successfully used as additinal components in the catalyst. Zinc oxide is particularly named. It is, however, necessary that the dehydrating component be present in excess over the methanol forming part.

The preferred catalyst giving the best results according to the present day development is a thoria-alumina two component catalyst.

Thorium carbonate and alumina are precipitated separately. The precipitates are washed, mixed and dried at 300° C. Dilute solution gives less dense catalysts. The apparent density of pure thoria catalyst is 1.6 - 1.8 (with concentrated solution 2.4 can be reached). The percentage of alumina based on thoria varies from 30 - 40%. Contents under 20% show no effect. Above 40% CH_4 formation becomes excessive.

The alumina-zinc oxide (1:1) catalyst does not give comparable yields, only 100 gm/m^3 feed are recovered, compared to 130 gm/m^3 feed with thoria-alumina. It is, however, possible to use a two stage operation and thus obtain almost the same result with the cheaper catalyst.

4. Operating Conditions. (see also ref. IV/3 and IV/4 at the end of this section).

The CO and H_2 are consumed approximately in the ratio $CO:H_2$-1:1.2 with most of the oxygen being removed as CO_2. The CO_2 content in the exit gas is approximately 30%.

The synthesis is carried out in a once through operation (no "Kreislauf") with the feed gas containing $CO-H_2$ in the ratio they are consumed.

70-75% Conversion is obtained at average space velocities of 1350 V/H/V (10 times higher than in ordinary F.T. operation). The tests were carried out in 15 mm. and 25 mm. tubes of chrome nickel steel or copperclad steel.

500 lit/hr. was the maximum feed used in the laboratory to date. For larger scale operation the use of superheated steam or molten salt was considered as a cooling medium.

4. Operating Conditions (Cont'd.)

(a) Influence of Temperatures.

The following table is based on operation at 1300 V/H/V and 150 atm. pressure; pure thoria catalyst.

	Product Distribution			
Temperature ° C	400°	425°	450°	475°
C_1 and C_2	4%	8%	13%	20%
C_3 and C_4	5%	9%	16%	29%
Iso C_4	11%	20%	28%	32%
Liquid Isoparaffins	55%	42%	23%	8%
Naphthenes	15%	15%	14%	5%
Aromatics	-	2%	4%	6%
Alcohols (oxygenated Comp.)	10%	4%	-	-
	100	100	100	100

With increasing temperature the spectrum moves toward lower boiling products, while the oxygenated products disappear to be largely replaced by aromatic compounds.

The reaction is not very sensitive to temperature change, ± 10° C are acceptable variations.

(b) Influence of Pressure.

The following table is based on operation at 450° C and 1300 V/H/V in a copperclad tube over pure thoria catalyst.

Yields are expressed in gm/m^3 ideal gas:

Pressure atmospheres	0	6	30	150	300	500
C_3 and n-C_4	-	-	5.1	9.1	20.4	16.0
Iso C_4	-	-	5.4	30.0	41.6	46.5
Gasoline and oil	-	Trace	16.1	29.7	37.4	40.5
	Trace		26.6	68.8	99.4	103.0

Use of chrome nickel tubes gave somewhat higher yields. The increased pressure and the correspondingly longer contact time increased the CO conversion. At the same time this increased conversion is not endangered

4. Operating Conditions (b)(Cont'd.)

b) carbon decomposition which is less (at a given temperature) at increased pressure.

There is a slight carbon deposition in the course of the synthesis which makes it necessary to burn off the carbon from the catalyst. This is done every 3 - 4 weeks with air or air-recycle gas mixture at the synthesis temperature.

5. Products.

The synthesis products obtained with this process are mostly low boiling isoparaffins with isobutane the largest individual component.

Based on operation at 150 to 450° C, 1300 V/H/V, and pure thoria catalyst the following product was obtained:
(Note: This is same test shown in the first table under 450° C temperature).

Composition of "gasol":

C_3	20%
i C_4	70%
n C_4	10%
	100%

(No butylene was found)

Composition of liquid Product:

Fraction (°C)	Component	% of Liquid
20 - 33°	Isopentane	11.8%
33 - 47.8°	n-Pentane	1.0
	Neohexane	0.2
	Undetermined	0.3
47.8 - 64°	Neohexane	13.6
	Undetermined	1.7
64.0 - 88.5°	Naphthene	2.9
	* Paraffin	9.6
88.5 - 98.0°	1,3 Dimethylcyclopentane	9.4
	Isoheptane	5.1

* Probably contains 2, 4 dimethylpentane.

(Cont'd.)

4. Operating Condition (b)(Cont'd.)

Composition of liquid Product:(Cont'd.)

Fraction (°C)	Component	% of Liquid
98.0 - 113.0°	Naphthene	7.8
	Paraffin	3.7
113.0 - 131.3°	Naphthene	7.7
	Paraffin	2.4
131.3 - 239°	Naphthene and Aromatic	22.3
	Paraffin	-
239°+	Solid residue	0.5
		100.0% of vol.

The Octane Number (motor method) of the gasoline fraction varies from 79 - 85 clear.

6. Conclusions.

The isosynthesis is of technical interest as a directed reaction of CO and H_2. By the use of particular catalysts and operating conditions, CO and H_2 can be combined to yield a hydrocarbon mixture consisting predominantly of isoparaffins.

The high temperatures and high pressure required for this synthesis would be a debit to its commercial use. As a fuel, the isosynthesis product would be of premium quality, but the components are otherwise of no special interest today.

7. List of References.

(1) Patent application by KWI dated 18 December 1942.
"Verfahren zur Kataytischen Syntheses von Kohlenwasserstoffen aus CO und H_2".

(2) Protocol of meeting, KWI and RCH, 2 June 1943.

(3) Progress report on development of Synthesis from CO and H_2 particularly synthesis of iso paraffins, by KWI, December 1942.

(4) Patent application by KWI dated 2 October 1943.
"Verfahren zure Herstellung von klopffesten Kohlenwasserstoffen".

THE SYNTHESIS OF HYDROCARBONS AND CHEMICALS FROM CO AND H_2

SECTION V

ISOBUTANOL SYNTHESIS

SUMMARY

The attached report covers information regarding the synthesis of isobutanol and higher alcohols by a modified h.p. methanol process.

The isobutanol synthesis was a prewar I.G. development and was practiced extensively for the production of isobutylenepolymer (appanol) and iso-octane. The high boiling fractions, while only a small percentage of the total product were of great interest for the production of detergents and lube oil esters.

1. Isobutanol Synthesis.

The following information on the synthesis of isobutanol was obtained from Dr. Goggel of the I.G. Farbenindustrie at the Ludwigshafen plant on 28 May 1943. This synthesis is in essence an extension of the high pressure methanol synthesis which utilizes carbon monoxide and hydrogen. The isobutanol synthesis uses the same raw materials, practically the same catalyst, and pressures of the same magnitude (about 240 atmospheres). The catalyst used for the higher alcohols in zinc and chromium oxides with the addition of one percent of potassium hydroxide. The temperature used is about 430° Centigrade.

The main difference compared to the methanol synthesis is the lower output per catalyst volume, since the main product (CH_3OH) is recycled to extinction. Based on a once-through operation, the product made in greatest quantity in this synthesis is methanol; about five to six parts of methanol are obtained for every part of isobutanol. In addition to this, there are a great many other alcohols and ketones produced. The total weight of these products equals the weight of isobutanol in the product.

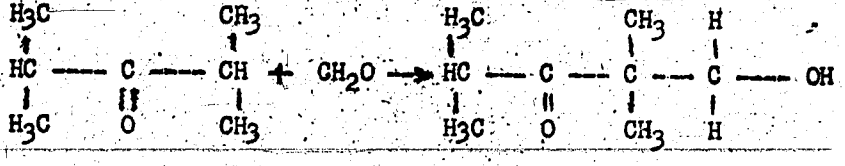
On a water free basis the total product contains approximately:

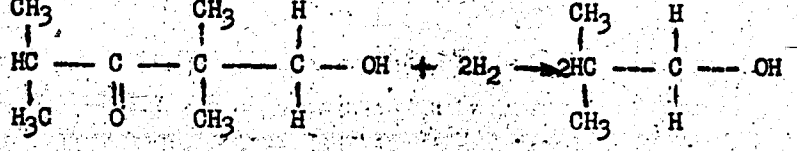
Isobutanol	14%
Methanol	63%

1. Isobutanol Synthesis (Cont'd.)

High alcohols and Ketones	15%
Hydrocarbons	5%

An important part of the isobutanol synthesis which increases the yield of isobutanol and utilizes one of the by-products is the reaction of "isobutyron" with formaldehyde to give 2 molecules of isobutanol. The "isobutyron" is apparently a misnomer and should more properly be called diisopropyl ketone. This reaction is as follows:

(a) 

(b) 

(See also reference V/6 at the end of this section).

The separation of the products from this synthesis is by fractional distallation. The equipment involved is not novel in any of its features, but is complex only because of the multi-component mixture which must be separated. The distallation scheme is straight forward, using continuous flow through columns which remove one component at a time. (see ref. V/1 to V/5 at the end of this report).

2. Details.

In the isobutanol synthesis a feed gas of approximately the following composition is used:

Carbon monoxide	32%
Hydrogen	57%
Nitrogen	Balance

2. Details (Cont'd.)

The catalyst is a pelleted catalyst made up of the following:

Zinc oxide	60 parts
Chromium oxide	40 parts
Potassium hydroxide	1 part

The zinc oxide is broken up and chromic acid is added. The mixture is worked 1/4 hour, then 0.5% graphite is added as lubricant. The mixture is then moistened with distilled water (300 kg. ZnO, 60 kg. Cr_2O_3, 20 lit. H_2O). A reaction occurs in 1/4 hour. The catalyst is then pressed into pellets 5-5 mm. 1% KOH is added to the final catalyst in form of fine K_2CO_3 powder. This is the only difference between isobutyl and methanol catalyst. The catalyst is charged to the chamber and reduced in the place. The conditions for the reaction are:

Pressure	240 atmospheres
Temperature	430° Centigrade

The composition of the gas leaving the converter is approximately as follows:

Carbon monoxide	22%
Carbon dioxide	5-6%
Hydrogen	57%
Nitrogen	5%
Hydrocarbons (mostly CH_4)	Balance

The analysis of the liquid product is approximately as follows:

Isobutanol	12%
Methanol	55%
Water	18-20%
High alcohols and Ketones	10%
Hydrocarbons	Balance

All methanol is recycled to the chamber. It is impure and purification cannot be economically justified. The recycle has no effect on the isobutanol yield. The methanol in the feed is considered simply like $CO + 2H_2$. A detailed listing of the compounds contained in the product is given here to illustrate the complexity of the composition. These are taken from the attached chart.

(a) Hydrocarbons, total about 5 per cent

Propylene	Diisobutylene
Propylcyclohexane	Triisobutylene

2. Details (Cont'd.)

(b) Alcohols - total about 70 - 75%

Methanol	Propanol
Ethanol	Butanol
n-amylalcohol	Isobutanol
Ethylisopropylcarbinol	Diisopropylcarbinol
Dimethylcyclohexanol	Sec.-butylcarbinol

Aldehydes - total about one per cent

Formaldehyde
Isobutyraldehyde
Diethylacetaldehyde

Ketones - total about 8 - 10%

Acetone
Methylethylketone
Methylpropylketone
Ethylisopropylketone
"Isobutyron" (Diisopropylketone)
etc.

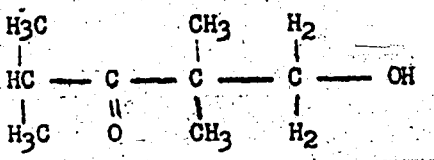
The balance if made up of acids, alctones, and phenols.

The condensation of "isobutyron" with formaldehyde is as follows; The materials are utilized in these ratios:

Material	Mols.
500 tons per month of 90% Isobutyron	3.95
500 tons per month of 30% Formalin	5.00
130 tons per month of 20% Sodium Hydroxide	0.65
500 tons per month of methanol (Solvent)	

These are charged batchwise to agitated autoclaves in such a manner that the sodium hydroxide catalyst is added over a period of 9 hours, while the temperature is maintained at 50° C. At the end of this period the crude condensation product is charged to a still in which the methanol is removed. The residue product from this distillation is washed with water to remove salts and the remaining formaldehyde, and is neutralized by the addition of sodium sulphide The washed crude product is then distilled to separate the unreacted "isobutyron" from the condensation methylol-isbutyron.

2. Details (Cont'd.)



The isolated methylol "isobutyron" is then hydrogenated over a copper chromite catalyst at 200 atmospheres and a temperature of 180 to 200° C.

The product is purified by a fractional distillation in which methanol is removed from the top of the column, pure isobutanol is taken off as side steam, and the high boiling residues are taken off at the sump.

About 400 tons per month of isobutanol are obtained from 500 tons of "isobutyron". This is a yield of about 62% of the theoretical.

The isobutylalcohol is dehydrated over alumina to isobutylene at 330 to 360° C. The best temperature gives 95% conversion and the operation is once through. No recycle is required. The alumina has a 3 - 4 month life.

Isobutylene was used for iso-octane production and as feed stock for oppanol (polyisobutylene).

While the isobutysynthesis was of importance during the war for the production of iso-octane, it was claimed that the process was equally of peacetime value as a producer of isobutylenes for oppanol and particularly for the higher alcohols boiling from 180 to 250° C. This fraction was used for the production of the "Zornol" (synthetic lubricants).

3. List of References.

(1) Schedule "Aus dem Isobutylöl isolierte Verbindungen".

(2) "Erfahrungs austausch über Roh Isobutylöl Destillation", by Hanisch, 25 January 1944.

(3) Flow sheet: "Isobutylöl destillation".

(4) "Unterteilung der gesteh-Kosten für die Roh-isobutylöl Produkte", IG Oppau, 27 November 1935.

3. List of References (Cont'd.)

(5) "Methanol und Isobutylöl destillation", 1939/1940 by Dr. W. Weber 1939.

(6) "Verfahren zur Herstellung von Isobutanol aus K-Fraktion"; Leuna, 30 November 1943.

SECTION IX

LOW PRESSURE METHANOL SYNTHESIS

Abstract

The attached report covers the development of a new synthesis of methanol which is carried out at 30 atmospheres as compared with the usual operation at 250 atmospheres. The work was carried out on a laboratory scale and had resulted in the assembly of a pilot plant at the Degussa laboratory at Wolfgang near Hanau.

In view of the large saving in equipment and operation this synthesis, if carried through to commercial realisation, may be of great interest to the producers of methanol in the United States.

1. Low Pressure Methanol Synthesis.

The following information on the synthesis of methanol, by utilisation of pressures not in excess of 30 atmospheres, was obtained during an interrogation of Dr. Brendlein of the Deutsche Gold-und Silber Scheideanstalt (Degussa) at the Wolfgang bei Hanau plant of the company. This synthesis uses as raw materials carbon monoxide and hydrogen. In this respect it is similar to the commonly used high pressure synthesis of methanol. The net reactions involved are shown in the following equations:

$$\text{I} \quad H_2C{=}CH_2 + CO \longrightarrow H-\overset{O}{\overset{\|}{C}}-O-CH_3$$

$$\text{II} \quad H\overset{O}{\overset{\|}{C}}-O-CH_3 + 2H_2 \longrightarrow 2\,CH_3OH$$

$$(\text{I}+\text{II})\quad CO + 2H_2 \longrightarrow CH_3OH$$

The catalyst for reaction I is sodium methylate dissolved in methanol, the catalyst for the second reaction is a typical hydrogenation catalyst described by Adkins, made up of copper, chromium and barium oxide. From the above set of equations it can be seen that although two molecules of

1. Low Pressure Methanol Synthesis (Cont'd.)

methanol are formed, one is recycled for reaction I and one is product so that the result is the combination of one molecule of carbon monoxide and two of hydrogen to give one methanol. Overall yields of 95% to methanol are claimed for the process.

Enclosed with this description are four reports which give in detail the experimental findings of this work. Report (a) gives the results of experimental batch processes; (b) confirms the findings of (a) and although other alcohols such as ethanol and butanol can be used in the synthesis in place of methanol, methanol is selected as the optimum reaction medium; (c) discusses methods of continuous operation with both counter-current and parallel flow of raw material through the reaction vessels; (d) describes the hydrogenation step (II) of the synthesis. In addition there are also enclosed two charts of which one shows in scheme the arrangement of the experimental equipment and the other shows in detail, the equipment and arrangement for a proposed plant to produce 28 tons per month of methyl formate or its equivalent of 15 tons of methanol.

2. Details.

Reaction I above is conducted as follows for a batch process:

Sodium metal, 5.8 grams, is dissolved in 100 grams of methanol; this makes approximately a 13% solution of sodium methylate. The solution is charged to an autoclave and air is removed by displacement with carbon monoxide, and then a pressure of 30 atmospheres is produced by feeding carbon monoxide. The temperature is raised to 80° C and as the carbon monoxide reacts the pressure is maintained at 30 atmospheres by feeding carbon monoxide. The temperature is held at 80° C. The yield of methyl formate in this step is about 38% of the theoretical. In continuous operation the yield of methyl formate is approximately 25% (see Report (C) above). The heat of reaction for step I is approximately 9 kilo Cal/mol. of methanol.

It is essential in this operation that the reactants be free of water and carbon dioxide, as either of these react with the catalyst as indicated below, so that if present in sufficient quantity, they will preclude the desired reaction:

(a) $CH_3ONa + H_2O \longrightarrow NaOH + CH_3OH$

TABLE I

Ester Fed.	Pressure Atm.	Temp. C°	Catalyst Load M/l/h	Ester fed g/h	Length of Expt., hours	% of Ester converted based on Ester fed	Yield of Methanol in % theoretical based on Formic acid
Ethyl Formate	30	210	3.68	41.0	7.0	90.5	85
Methyl Formate	30	215	4.74	42.6	5.75	97.8	58.4
Methyl Formate	30	200	5.42	48.8	7.1	97.7	62.9
Methyl Formate	30	200	4.34	39.0	8.0	96.3	66.2
Methyl Formate	30	180	4.41	39.8	7.75	96.3	83.5
Methyl Formate	30	160	4.34	39.0	7.5	97.4	94.5
Methyl Formate	30	160	13.43	121	7.1	95.7	95.5
Butyl Formate	30	208	2.65	42	7.0	87.6	80
Butyl Formate	30	200	2.94	44.7	7	92.8	90

1. Low Pressure Methanol Synthesis (Cont'd.)

(b) $NaOH + CO \longrightarrow HC(=O)ONa$

(c) $CH_3ONa + CO_2 \longrightarrow CH_3OC(=O)ONa$

The presence of hydrogen in the carbon monoxide used in this step tends to decrease the yield of methyl formate. It is not essential, however, that the hydrogen be removed completely, because experiments with acceptable yields have been made with carbon monoxide containing 30 volume percent hydrogen.

The crude product from the addition of carbon monoxide to methanol is separated from the catalyst salts by distillation of methanol and methyl formate and is then hydrogenated. The apparatus used in the hydrogenation was a silver plated tube of 175 cc volume containing 150 cc of Adkins catalyst of copper-chromium-barium oxide. The tube was 40 cm. in length. Thermocouples were placed along the tube. The temperature in this step is closely controlled between 175 and 185° Centigrade. Higher temperatures give rise to two side reactions, one of which decreases the yield of methanol but does not decrease the efficiency in that the products are methanol and carbon monoxide which can be recycled in a large installation. This reaction is indicated as follows:

$$HC(=O)OCH_3 \longrightarrow CH_3OH + CO$$

The second reaction, which results from too high a hydrogenation temperature, not only decreases the yield but also decreases the efficiency in that the products are not adaptable to further utilization.

$$HC(=O)OCH_3 \longrightarrow CH_4 + CO_2$$

The yields obtainable in the hydrogenation step are indicated in the following table taken from Enclosure (A) mentioned above.

The products of the hydrogenation are separated by fractional distallation. The distillation is not complicated in that the products boil at widely different temperatures, methyl formate 31.8° C, and methanol 64.7° C. No azeotropes are formed in the fractionation.

3. List of References.

The German documents listed below are available in the library of the Bureau of Ships in Washington, D.C.

(1) Four sections (I to IV) of report:
"Mitteldruck Methanol Synthese/Zweistufen Verfahren" -
by Dr. Brendlein, Date 16 November 1942
17 March 1943
21 October 1943
18 November 1943

(2) One drwg: Flowsheet "Methanolsynthese"

(3) One drwg: Degussa 16159 "Schema Versuchsanlage M2"

(4) "Methylformiat aus CH_3OH and CO" by Dr. Pohl, 14 February 1944.

(5) "Betriebsbeschriebung zur Herstellung von 28 Moto Methylformiate", by Dr. Brendlein, 8 June 1943.

(6) "Mitteldrucksynthese in Vergleich Zum Hochdruckverfahren der I.G." - by Dr. Brendlein, 4 December 1943.

(7) One Letter by Prof. Dr. O. Fuchs re: Methanol Synthesis addressed to Dr. Brundi, 15 May 1943.

(8) One Folder: File on Patent Application by Degussa: "Verfahren zur Herstellung von aliphatischen Estern"

THE SYNTHESIS OF HYDROCARBONS AND CHEMICALS FROM CO AND H_2

SECTION VII

THE OXO-SYNTHESIS

SUMMARY

The attached report covers the development of a new synthesis of higher boiling alcohols by reacting olefines with CO and H_2 over cobalt catalyst at 150 atm. The development was carried through laboratory and pilot plant stage and resulted in the erection of one 10,000 ton/year plant by Ruhrchemie AG at Holten.

Contents.

SECTION VII

THE OXO-SYNTHESIS

1. General Introduction. (see ref. VII/1 and VII/2 at the end of this section).

Oxo-synthesis is a process for the production of alcohols by the reaction of olefines with one molecule each of CO and H_2 and subsequent hydrogenation of the resulting aldehyde.

The process was developed independently by Ruhrchemie and I.G. Farben. During the war these companies arrived at an agreement whereby they would pool their information, but up to this time only one commercial plant has been erected (by "Oxogesellschaft"m.b.H. at Holten). The unit was never started and thus no actual plant performance data are available. All information given below is based on large scale pilot plant operation and laboratory work.

The Ruhrchemie plant is based on a batch type operation, while I.G. Leuna had developed a continuous sump-phase type process. It is felt that the I.G. process is ready to be put into commercial practice and is superior to RCH. The main improvement consists in the continuous operation and somewhat higher output per catalyst volume.

The principles involved and their practical application are described below:

2. Chemistry of the Oxo-Synthesis. (See ref. VII/3, VII/5 to VII/7 at end of this sect.)

The following reactions occur when olefines are contacted with $CO-H_2$ mixtures over certain catalyst:

(a) Primary Reactions.

(1) Formation of aldehyde

$$R-CH=CH_2 + CO + H_2 \longrightarrow \begin{cases} R-CH_2-CH_2-CHO \\ R-\underset{\displaystyle HCO}{\underset{|}{CH}}-CH_3 \end{cases}$$

(2) Formation of Ketone

$$2RCH=CH_2 + CO + 2H_2 \longrightarrow \begin{cases} R-CH_2-CH_2-CO-CH_2-CH_2-R \\ R-CH_2-CH_2-CO-\underset{\displaystyle CH_3}{\underset{|}{CH}}-R \\ R-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CO-\underset{\displaystyle CH_3}{\underset{|}{CH}}-R \end{cases}$$

2. Chemistry of the Oxo-Synthesis (Cont'd.)

(b) Secondary Reactions.

(1) Formation of acid: analogous to 1a. using H_2O instead of H_2.

(2) Formation of paraffin: hydrogenation of olefine feed (does not occur under synthesis conditions).

(3) Formation of carbonyl: from catalyst and CO.

A great deal of work has been done to study these reactions and some of the results are listed below:

Pure olefines of different types were subjected to the Oxo reaction and the products separated and each chemical individual analyzed in detail.
For example: pure 2 methylpentene - 1 (Isohexane)
pure dodecylene - 1
pure cyclohexene.
were reacted with $CO + H_2$. The catalyst was removed and the CO-carbonyl decomposed by washing with 5% H_2SO_4. The products were then analyzed. (Note: that this is only the first step of the oxo-synthesis). The aldehydes are not easily analyzed since they are highly reactive. It is known that more alcohols are usually formed in the oxo synthesis than would be expected from the analytical determination of the aldehydes after the first step.

(c) Products from 2 Methylpentene - 1

45% of product boiling below 200° C (760 mm.) identified in this fraction were:

3 methyl hexylaldehyde (main product)
3 methyl hexylol
3 methyl capronic acid

In the higher boiling fraction the following products could be found:

2, 8 dimetheyl-undecanone - 6
Higher ester of 2-methylcapronic acid.

These products correspond exactly to the basic reactions listed at the beginning of this chapter.

2. Chemistry of the Oxo-Synthesis (b)(Cont'd.)

In parallel fashion cyclohexene was treated and the following identified in the products:

hexahydro - benzaldehyde
dimer of " "
trimer of " "
hexahydro benzyl alcohol
hexahydro benzoic acid - hexahydro benzyl - ester.

The compounds charged to Oxosynthesis, particularly those obtained from F.T. type operations are known to be substantially terminal olefines. Yet it was found that some of the products could have been formed only if a double bond shift had preceded the formation of the aldehyde. This effect was studied and the results are summarized below:

Again n-dodecylene - 1 was used as starting material, and subjected to Oxo synthesis. But the reaction was carried through to the alcohol. In order then to establish the structure of the alcohols, they were first carefully dehydrated and the olefine was next split by oxidation and treatment with Ag_2O. The resulting acids were checked for their chain length and thus the branching was determined, which could only be an effect of a shift of the double bond of the n-dodecylene - 1 feed during the Oxo-reaction.

These tests proved, that from terminal normal olefines the oxosynthesis yields branched alcohols, in particular 2-alkyl alcohols, whereby the yield decreases with increasing length of the sidechain.

It was finally possible to prove that cobalt carbonyl was the catalyst responsible for the double bond shift. Dodecylene - 1 was treated at 150 to 200° C and 200 atm. of CO and with Co-thoria catalyst and all isomer dodecylenes were found in almost equimolecular ratio.

Fe-carbonyl showed a similar effect, but not the same activity, as only 40 to 45% of the dodecylene - 1 was isomerized. Nickel however, had no effect at all. These findings are interesting because the three named metals catalyze the Oxo reaction in about the same extent as they isomerize the double bond.

The shift of the double bond was made the subject of a patent application by I.G. Farben. (See reference VII/9 at end of this section). The disclosure involves the treatment of olefine hydrocarbons with

2. Chemistry of the Oxo-Synthesis (c)(Cont'd.)

metalcarbonyl (particularly cobalt-carbonyl) at 70 atm. CO pressure and at 150° C for two hours with 3% catalyst in the feed as an example. The process should serve to raise the octane number of the hydrocarbon. (Note: that similar tests were carried out on synololefines, which were to be used as feed stock for the Oxo-synthesis). The olefines were found to be at least 90% straight chained.

The Synololefines, on the other hand, are not necessarily all terminal olefines. These facts seem to constitute the proof that the Synol reaction (for alcohols) does not consist in an Oxo type synthesis carried out on initially formed olefines. If such were the case, the synol alcohols would have to contain about 50% α-substituted alcohols, which they do not. Much rather it is possible that they (synol olefines) are the result of a dehydration of the primarily formed terminal alcohol, followed by a shift of the double bond.

That Fe has a tendency to shift the double bond, was seen from the analysis of a Synol fraction (undecylene: 73°– 78° C at 10 mm. Hg.) which had been synthesized over the standard iron catalyst:

Undecylene	D1	D2	D3	D4	D5	D6
Mol. %	60	27	2	1	0	

This compares as follows with the distribution of the double bond, obtained from n-dedecylene-1 by treatment with $Co(CO)_4$

Dodecylene	D1	D2	D3	D4	D5	D6
Mol. %	8.1	27.2	23.0	18.1	13.3	10.3

3. Olefines for the Oxo Reaction.

The following materials were considered as feed for the oxo-synthesis:

Olefines from Fischer oil (Kreislauf operation)
" " Cracked Fischer wax
" " Fe catalyst F.T. operation
" " Synol operation
" " Various cracked mineral oils
" " Shale oils
" " Hydrogenation products.

It appears that the reaction is applicable in principle to all monoolefines independent of origin. The limitations probably arise from the

3. Olefines for the Oxo Reaction (Cont'd.)

impurities contained in the olefines, such as aromatics, gums, or catalyst poisons. It is for this reason, that synthetic olefines are preferred, but good results were obtained from mineral oil olefines in spite of their sulphur content. The temperature required for the synthesis is somewhat higher and the sulphur content is a drawback in the hydrogenation stage, unless it is carried out quite independently over sulphide catalysts.

Olefines containing charging stocks from different synthesis operations were studied extensively, to evaluate their use for the oxo reaction. The following products were tested:

	Catalyst used in synthesis
Ruhrchemie, primary synthesis olefines	Cobalt
Ruhrchemie, thermally cracked wax	Cobalt
Synol-olefines	Iron
Michael (I.G. "Schaumfahrweise") olefines	Iron
Lurgi olefines	Iron

The conclusions were as follows:

(1) In all cases over 95% of the olefines are converted

(2) The cobalt products are more uniform and contain only olefines, paraffins, and alcohols.

(3) The Fe-products contain sizeable amounts of acids, esters, aldehydes, etc., and are rendered more uniform by oxo operation (due to the hydrogenation).

(4) The total alcohol concentration in the final product is lower in the cobalt produced olefines and reaches a mixmum in the synol product.

(5) The usefulness of the alcohols for detergents is less in the case of iron synthesis, since the chain length is somewhat shorter.

In order to compare the different synthesis fractions for the oxo-synthesis, the following table has been prepared: (See attached sheet)

Special Feed Stocks:

It was attempted to apply the oxo reaction on other compounds containing double bonds, with the following results:

3. Olefines for the Oxo Reaction. Special Feed Stocks (Cont'd.)

Tetra methylautadiene:	Reaction only with one double bond
Dimethylhexadiene:	Only 40% of expected product; rest is hydrogenated at one double bond, while other reacts according to Oxo reaction.
Allylalcohol:	Reaction products very complex. No detailed analysis available.

4. Catalyst for Oxosynthesis.

The catalyst is identical with the standard cobalt Fischer-Tropsch catalyst. It is applied as a slurry in the liquid feed. Usually in concentration of 3% wt. catalyst based on olefine in the feed. At the end of the operation the catalyst if filtered from the reactants through a ceramic disc or thimble and returned for further use. About 100 batches can be processed with one catalyst charge.

The catalyst contained cobalt, thoria, kiesleguhr in the customary ratio 100-1.5-200 (weight %). It did not contain magnesia, because it was found that MgO encouraged condensation of aldehydes. The catalyst had an apparent density of 0.3 to 0.35. Thus 10 kg. of oil contained about one liter of the catalyst. RCH used batch operation and carefully avoided all pumping of the slurry. The liquid was removed from one vessel to another by gas displacement. In the continous operation used by I.G. it was found that the kieselguhr caused considerable trouble due to abrasion in the pump valves. Attempts to replace the kieselguhr with talcum failed.

One of the main problems in the process is the formation of cobalt carbonyl. (Its effect on the double bond has already been described). I.G. Leuna developed a cobalt- copper catalyst, which gave only a fraction of the carbonyl (less than 10 milligram/liter). The copper has a stabilizing effect on the cobalt. This catalyst was satisfactory for the 1st stage (aldehyde formation) but did not hydrogenate well.

The activity of the standard catalyst for the 2nd stage (hydrogenation) is considerably diminished by the presence of even small quantities of CO in the hydrogen. This sensitivity becomes more pronounced with the age of the catalyst. The installation of a "Methanizer" was therefore considered to remove this residual - CO from the H_2-cycle in the 2nd stage.

TABLE II CONTENT OF OLEFINES AND OXYGENATED COMPOUNDS OF VARIOUS SYNTHESIS PRODUCTS

Fraction °C.	Number of Carbon Atoms	"Kreislauf" middle oil		RCH therm. crack-wax		Synol "Benzin-Fahrweise"		Synol Alcohol Operation		Michael Synthesis Product		Lurgi Synthesis Product	
		Olefine	Oxygtd Compds	Olefine	Oxygtd Compds	Olefine	Oxygtd Compds	Olefine	Oxygtd Compds	Olefine	Oxygtd Compds	Olefine	Oxygtd Compds
105-175	8-10	42	16	80	0	-	-	17	65	-	-	-	-
175-218	11-12	41	10	80	0	46	20	18	68	46	36	52	7
218-255	13-14	33	9	75	0	47	21	16	68	48	25	55	5
255-290	15-16	28	9	50	0	43	21	16	68	45	12	50	4
290-320	17-18	20	11	40	0	42	20	18	69	40	14	45	7
320-360	-	15	5	-	-	45	18	17	59	32	20	-	-

All values are weight %

Note: that the Oxygenated compounds include alcohols, aldehydes, acids and esters. For detail breakdown, see attached German report.

See also Reference VII/5 at end of this section.

4. Catalyst for Oxo-Synthesis (Cont'd.)

Another modification of the continuous process had been developed by I.G. Farben at Ludwigshafen. (See also reference VII/17 at end of this section). In this process cobalt acetate is contacted with fatty acids (from Oxo-alcohols) in an autoclave to yield the cobaltsalt of the fatty acid. (The free acetic acid is condensed).

Thus the cobalt is introduced in solution into the feed to give a 0.02 - 0.05% Co concentration. This mixture is charged to the reactor where it passes over a solid cobalt catalyst bed (Co on pumice). The mixture is finally freed from the cobalt in a special smaller reactor, which is filled with plain pumice. Hydrogen is added here and the reduced cobalt deposited on the pumice. After several months the final reactor must be purged of cobalt. This is done by CO, which forms carbonyl; the carbonyl is again dissolved in oil and returned to the feed.

This process does not require any filtration step. The gas streams of the process must be continuously checked for Co carbonyl. It is necessary to control its decomposition, or if possible, direct it to a part of the plant where it does no harm. In general, it is scrubbed out in a wash column using the olefine feed as sponge. Cobalt deposition throughout the plant due to Co carbonyl has been a considerable problem in the continuous process.

The catalyst, as any F.T. catalyst, must be reduced. In the particular case of the oxo-synthesis, where a slurry is used instead of a solid bed, the pelleting of the catalyst is unnecessary. This however, calls for some special arrangement to reduce the catalyst. It could be pelleted, reduced, and again broken up, but the I.G. engineers proposed reduction in "fluid phase". In a patent application dated 9 July 1942, the use of a funnel shaped vessel was disclosed for the reduction of catalyst powder, (See reference VII/8 at end of this section) where the reducing gas would keep the dust in motion. A filter or other means could be used to remove the catalyst from the gas stream which was recycled through the catalyst.

5. Operating Conditions.

(a) RCH Batch Process.

The total olefine feed ($C_{11}+$) boiling from (175 to 303° C) is first fractionated into narrow cuts. This is necessary for the subsequent

5. Operating Conditions (a)(Cont'd.)

separation of the products into the neutral oil and the alconols. The latter, having been lengthened in their chain by one carbon atom, boil 20 to 30° C above the corresponding olefine. All distillations in the oxo plant must be done carefully and the different unavoidable intermediate fractions are either rerun or discarded. If this rule is not followed the final alcohol product is contaminated with undesirable products.

The C_{11}-C_{17} feed is fractionated into the following four fractions:

$C_{11}C_{12}$	175 - 218°	45%
$C_{13}C_{14}$	218 - 245°	25%
$C_{15}C_{16}$	245 - 280°	20%
C_{17}+	280 - 305°	10%

(The feed is obtained from LP and MP cobalt synthesis and thermal cracking of "Gatsch".)

The fractionation was carried out under atmosphere pressure for the first two cuts and under 100 - 150 mm. Hg. vacuum for the last two. "Kittel" columns were used, with 10:1 reflux ratio. They were chosen because they were considered to give less pressure drop through the tower and thus allowed a bottom temperature several degrees below that required by ordinary bubble towers.

All four fractions were treated alike in the oxo plant as follows:

A known volume of feed was mixed with 3.0 - 3.5% by weight of the catalyst. The slurry was pressured into the tubular reactor and watergas ($CO:H_2$ = 1:1, purified) introduced at 150 atm. The reaction is exothermic by 45 kg. cal/kg. of olefine. The heat of reaction is removed by the cooling coil. In addition the pressure may serve as a means to control the heat release. (By lowering the pressure the reaction is slowed down).

The gas is pumped through the reactor in a closed recycle. As the reaction proceeds and gas is used up, the pressure drops. New gas is added and the reaction is complete when no further drop in pressure occurs.

Throughout the reaction a temperature between 125 and 140° C is maintained, depending on the type of feedstock. The temperature may be raised towards the end of the reaction to encourage decomposition of the

5. Operating Conditions (a)(Cont'd.)

carbonyl. The watergas is then released and the entire batch including the catalyst is pressured into the (2nd stage) hydrogenation chamber. The olefines are converted 100% in the "aldehyde" stage. 87 - 95% go to aldehyde, yielding about 100% wt. of alcohol based on olefine fed. The rest goes to ketone and aldol, but the latter are largely broken up in the hydrogenation to give additional alcohol.

The hydrogenation is also exothermic by about 30 - 35 kg/cal kg/mol. hydrogen reacted. The operation is carried out in analogous fahion to the aldehyde step. Pure hydrogen is admitted at 150 atm. The H_2 is recycled until no further pressure drop occurs. The temperature is held at 180° C. At the end of the reaction the H_2 is released and the product withdrawn. The catalyst if filtered through a ceramic thimble.

Before final distillation the product is caustic washed to remove the acids formed in the process. The distillation is carried out in batch columns. Care is to be taken that the kettle temperatures do not exceed 180 to 200° C (about 5 mm. Hg. is required in the higher fractions). Aluminum was used in the construction of the coolers and receivers of the fractionating system (See also reference VII/15 at end of section).

The distillation of the two lower boiling feed fractions ($C_{11,12}$ and $C_{13,14}$) is carried out in one column each. The "neutral" oil and the alcohol are taken overhead in succession. The two higher boiling feed fractions ($C_{15,16}$ and C_{17}) are distilled in two towers each. The neutral oil is removed first and the alcohols in the second tower. The heavy polymers from all four fractions are charged to a common evaporator. Refractive index measurements are used in the distillation to control the overhead cut points. The difference in b.p. between alcohol and paraffin is 1.39 to 1.42.

The gas requirements for oxo-synthesis are given as follows: (they are substantially the same for all types of operation)
Basis 10,000 ton/year of alcohol:

	Watergas	Exit gas 1st stage
CO_2	6.8%	12.9%
CO	38.0%	27.3%
H_2	49.0%	48.1%
CH_4	0.2%	0.4%
N_2	6.0%	11.3%

5. Operating Conditions (a)(Cont'd.)

	Watergas	Exit gas 1st stage
	5,145,000 m^3/year	2,715,000 m^3/year *
	Hydrogen	Exit gas 2nd stage
H_2	90%	85%
N_2	10%	15%
	3,633,000 m^3/year	2,418,000 m^3/year *

* This is on once through basis. (See also reference VII/25 at end of section.)

(b) I.G. Leuna.

The I.G. Leuna type of operation was continuous. It might be pointed out that RCH would probably also have gone over to a continuous operation in the near future. The fresh feed is used to pick up the catalyst from the ceramic filter and is charged to a mixer, where fresh additional catalyst can be added. The slurry is then picked up by the h.p. feed pump and pumped through a preheater in the reactor proper. Watergas is recycled through the reactor at 150 atm. Cooling tubes in the reactor are used to remove the heat of reaction. The slurry is next withdrawn and the pressure released in a gas separator. The gas is passed through a scrubber, where cobalt-carbonyl is removed by washing with fresh olefine feed. The slurry from the gas separator is fed to the hydrogenation system, which is an exact duplicate of the one described above. Pure hydrogen is used instead of watergas. The slurry from the final gas separator is filtered and the filtrate caustic washed, before refractionation.

Details of the operation may be taken from the attached documents.

(c) I.G. Ludwigshafen.

The system was described in the paragraph on catalyst. It is in principle identical with the Leuna system except for the handling of the catalyst.

6. Operating Costs.

The cost of the HP section of the plant is approximately 35.RM/1 yearly ton alcohol. This however does not include the gas preparation,

6. Operating Costs. (Cont'd.)

compression plant and the utilities.

The labor requirement for a 15,000 ton/year unit were given as 50 men/shift (based on batch operation). This includes all operating and maintainance labor.

The Utilities are given below:
Basis: 15,000 ton/year alcohol from $C_{11}-C_{17}$ with 30% olefine content in feed.

Heating Requirement:

Distillation	320,000 kg cal/hr
Gas preheater - 1st stage	13,500 "
" " 2nd stage	16,500 "
Methanizer	31,000 "
Losses	40,000 "
	421,000 kg cal/hr

Cooling Requirement:

Synthesis, 1st stage	100,000 kg cal/hr
" 2nd stage	52,500 "
Product cooler, 1st stage	120,000 "
" " 2nd stage	150,000 "
Final cooler	90,000 "
Gas cooler	60,000 "
	572,500 kg cal/hr

Power Requirement: 100 KWH

The operating cost was given based on 1 Kg. alcohol (for 15,000 ton/year plant).

Power	0.04 RM/kg alcohol
Labor	0.03 "
Laboratory	0.01 "
Materials	0.01 "
Feedgas	0.03 "
Amortization	0.06 "
	0.18 RM/kg alcohol

At Ruhrchemie the cost of the olefine in the feed was calculated at 0.43 RM/kg. Thus the price of the final product would be 0.60-0.65 RM/kg Alcohol.

7. Conclusions.

The oxo-synthesis is the second of three major different processes for the production of high boiling alcohols. The great effort put into its commercial realization is due to the shortage of all kinds of soaps and detergents in Germany. Another important use for the product would have been its application in lubricating esters.

The development of the process may lead to continuous operation and possibly better control of the synthesis, such as suppression or closely controlled shift of the double bond to give clearly defined α-substituted alcohols of predetermined branching.

8. List of References.

The German documents listed below are available in the library of the Bureau of Ships in Washington, D.C.

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2. "Der derzeitige Stand des Oxo problems" - by Dr. Wenzel, 10 February 1942.
3. "Die Konstitutionder Oxo Alkohole" - by Dr. Asinger, Berg, April 1943.
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7. "Uber Reaktionsprodukte des Oxo Verfahrens" - by Eckhardt, 25 February 1942.
8. I.G. Patent Application; 9 July 1942 "Verfahren zur Reduktion staubförmiger Katalysatoren"
9. I.G. Patent Application; 11 September 1942 "Verfahren zur Verschiebung der Doppelbindung"
10. "Wassergas und H_2 Bedarf der Oxo Synthese" letter by Dr. Landgraf 17 December 1942.
11. Memorandum on Oxo-meeting, 10 February by Dr. Wilke, Herold.
12. "Oxo Verfahren" - 29 March 1943, letter I.G. to RCH.
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15. One drwg. Bamag-Meguin: 11E/10021 "Fliessdiagramm für destillation - Ruhrchemie A.G."
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20. One drwg. Merseburg M3463-16 "Fliesschemen für 50,000 Jato Oxo-Verfahren"
21. One drwg. "Schema d. Kontinuierlichen Fahrweise des Oxo-prozesses, Stand vom 1 May 1942."
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22. "Gesichtspunkte zum Bau nener Oxo Aulagen" - by Wenzel 30 March 1942.
23. Memorandum to Meeting 28 March 1942 by Metzger.
24. Memorandum to Meeting "Planung des Oxo-Verfahren" - by Gemassmer 11 May 1940.
25. Memo Re: "Energieverbrauch, etc. für Oxo-Aulage" - by Gemassmer, Mauthner, 7 July 1943.
26. "Die Herstellung Höherer Alkohole aus Olefinen" - by Grimme, Campen, (Rheinpreussen) 6 December 1943.

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