V. CHEMICAL AND PHYSICAL CHANGES DURING AN INDUCTION PERIOD

For any catalyst there is an induction period in which the as-prepared catalyst undergoes chemical changes to, it is desired, attain a steady-state composition during a long-term synthesis operation. In this section the induction period is considered to be that period in which the catalyst is preconditioned prior to the introduction of the synthesis gas and during the period of operation with synthesis gas that leads to the steady state conversion conditions. In general, it appears that the changes that occur during the induction period depend upon the preparation method for the catalyst, such as fused, precipitated, supported, etc. Furthermore, the changes following exposure to the synthesis gas depend upon operating conditions, and especially upon the conversion level. In the following section, a brief review will be given of: (1) the results from work in Germany, especially during WWII, that pertain to the induction period, (2) results obtained at the Bureau of Mines (and its subsequent organizational names), (3) reports from SASOL, and (4) appropriate open literature studies by other organizations.

V.1. FORMATION OF IRON CARBIDES

Hofer (V-1) made an attempt to correlate the more reliable of the existing data of interest in connection with the Fischer-Tropsch synthesis. He pointed out that metallic carbides can be conveniently classified under two general headings - the ionic (salt-like) carbides and the nonionic (interstitial) carbides. All of the catalysts used in the Fischer-Tropsch synthesis appear to form carbides of the interstitial type. The nonionic, interstitial type fall naturally into two subgroups - these are conveniently called the stable and unstable carbides. The stable carbides exist to high temperatures (4,000°C and above) and frequently will melt without decomposition. On

the other hand, Fe_2C, a member of the unstable group, is certainly metastable between 600 to 1,000°C with respect to iron and carbon.

Hofer (V-2) reports that only high surface area materials (at least 10 m^2/g) permit the formation of iron carbide directly from alpha iron at rates which are measurable by ordinary gravimetric procedures. Hofer indicates that the detailed mechanism of carbiding of alpha iron is somewhat uncertain but that the main features are as indicated in Figure V-1. For CO pressures of several atmospheres and

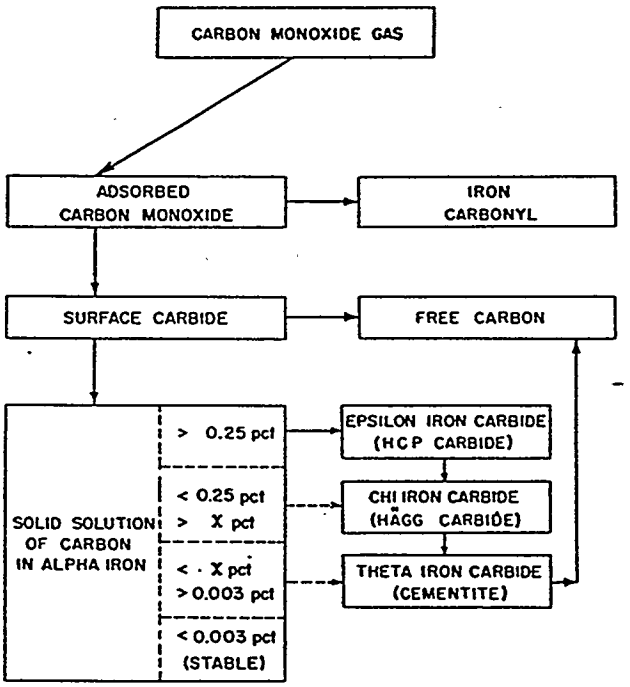


Figure V.1. Sequence of steps in the direct carburization of alpha iron. Heavy arrows indicate the most probable sequence (from ref. V-2).

temperatures above 100°C, iron carbonyl ($Fe(CO)_5$) is formed. At higher temperatures and lower pressures, CO dissociates on the surface to form chemisorbed O and C. The chemisorbed O reacts with a gaseous or chemisorbed CO to produce CO_2. The surface carbide atoms may form free carbon on the surface or penetrate the surface

to form a carbide. Which carbide is formed depends upon the temperature. Epsilon carbide (ϵ-Fe_2C, hcp) is formed at low temperatures, chi iron carbide (Hägg carbide, χ-Fe_2C) at intermediate temperatures and theta iron carbide (cementite, θ-Fe_3C) at high temperatures. Thus, Hofer et al. (V-3) found chi, but not epsilon, iron carbide when a reduced fused synthetic ammonia-type catalyst was carbided at 240°C. They found epsilon iron carbide as the principal product when a precipitated, copper-promoted catalyst was carbided at 190°C. Carbiding at 350°C produced theta iron carbide. Podgurski *et al.* (V-4) reported that an epsilon iron carbide could be formed with only partial carbiding at 215°C. The data in Figure V-1 indicate that the solution of carbon in alpha iron will not decompose to epsilon iron carbide unless the carbon in the solution is in excess of 0.25%. Cementite will not precipitate from a solid solution of carbon and alpha iron if the carbon concentration is less than 0.003%. Since chi iron carbide is intermediate in thermodynamic stability between the epsilon and theta iron carbides, an intermediate concentration of carbon in alpha iron must be the minimum necessary for chi iron carbide formation. Thus, the concentration of carbon in alpha iron in equilibrium with chi iron carbide must lie between 0.25 and 0.003%. In Figure V-1 the reaction sequence - solid solution → epsilon iron carbide → chi iron carbide → theta iron carbide - is represented by the solid arrows.

Hofer (V-2) concludes that at temperatures below 170°C, CO reacts quantitatively with alpha iron to form epsilon iron carbide and does so with no detectable free carbon. Between 170 and 230°C, CO reacts with alpha iron to form increasing proportions of chi iron carbide and decreasing proportions of epsilon iron carbide so that near 230°C no readily detectable amount of epsilon iron carbide can be demonstrated, and the alpha iron is converted quantitatively to chi iron carbide. At

temperatures above 230°C and below about 300°C, CO reacts with alpha iron to form chi iron carbide with possible traces of epsilon iron carbide; in addition, free carbon is formed as well. The carbon formed at these higher temperatures is nearly amorphous showing only a broad 002 peak in the XRD. Above 300°C the rate of carbon deposition is so rapid that it is comparable to or exceeds the rate of carbide formation. Cementite is sometimes reported for materials exposed to CO above 300°C.

Solid state reactions also can occur (V-2). In the absence of a gas phase, the sequence of reactions (we have written ϵ'-$Fe_{2.2}C$ and χ-Fe_5C_2 in place of ϵ-$Fe_{2.2}$ and χFe_5C_2 used in reference V-2):

$$\epsilon\text{-}Fe_{2.2}C \rightarrow \chi\text{-}Fe_5C_2 + C \qquad [V\text{-}1]$$

$$3\ \chi\text{-}Fe_5C_2 \rightarrow 2\ \theta\text{-}Fe_3C + C \qquad [V\text{-}2]$$

can be observed as isothermal reactions. First, ϵ-Fe_5C_2 is prepared at 170°C without residual α-Fe. At 230°C, ϵ'-$Fe_{2.2}C$ converts to χ-Fe_5C_2 at measurable rates. χ-Fe_2C can be prepared without residual α-Fe at temperatures below 230°C, and this material can be converted to cementite at temperatures above about 420°C. It is stated that these reactions occur by mechanisms of nucleation and growth.

ϵ'-$Fe_{2.2}C$ decomposes to χ-Fe_5C_2 in the same temperature range and at the same rate whether α-Fe is present or not. However, the presence of α-Fe causes the transformation of χ-Fe_5C_2 at a lower temperature and at a more rapid rate than when it is absent. Different reactions are involved in these cases, as shown in the following equations:

$$\epsilon\text{-}Fe_5C_2 + \alpha\text{-}Fe \rightarrow \theta\text{-}Fe_3C \qquad [V\text{-}3]$$

$$3\ \chi\text{-}Fe_5C_2 \rightarrow 2\ \theta\text{-}Fe_3C + C \qquad [V\text{-}2]$$

Thus, the presence of α-Fe prevents the formation of free carbon. The reaction of α-Fe with ϵ-Fe_5C_2 is the more rapid of the above two reactions; hence, the second reaction to produce free carbon can only occur in fully carburized systems.

Hofer (V-2) reported that up to 1966 little work had been done on the action of CO on iron oxide. The results of a study at the Bureau of Mines indicate that the direct carburization of iron oxide with CO did not produce as well defined a carbide as is formed by carbiding after prior reduction.

Hofer (V-2) reports, and many have shown the same result for high temperature conversions, that the action of CO on metallic iron forms carbon deposits that are in the form of long, tiny filaments about 0.1 micron in diameter and a micron or more in length. Near the midpoint of the filament is located a different material, presumably an iron carbide.

To make χ-iron carbide (Hägg carbide) from fused iron catalyst (D3001) by treatment of the reduced catalyst with pure CO (space velocity, 100 per hour), the carbiding temperature is increased from 150 to 350°C at such a rate as to keep the CO_2 content of the exit gas at 20%. Approximately 20 hours are needed to incorporate carbon to correspond to approximately Fe_2C. This method minimizes the deposition of free carbon and oxidation of the catalyst. Gas of composition H_2:CO = 1:4 can also be used (V-5).

Two methods, both at atmospheric pressure, are recommended for preparing cementite, Fe_3C (V-6):

1. the reduced catalyst is carburized with CO until 2/3rds of the Fe is converted to Hägg carbide; this mixture is then heated to 475°C in helium and held at this temperature for 2 hours.

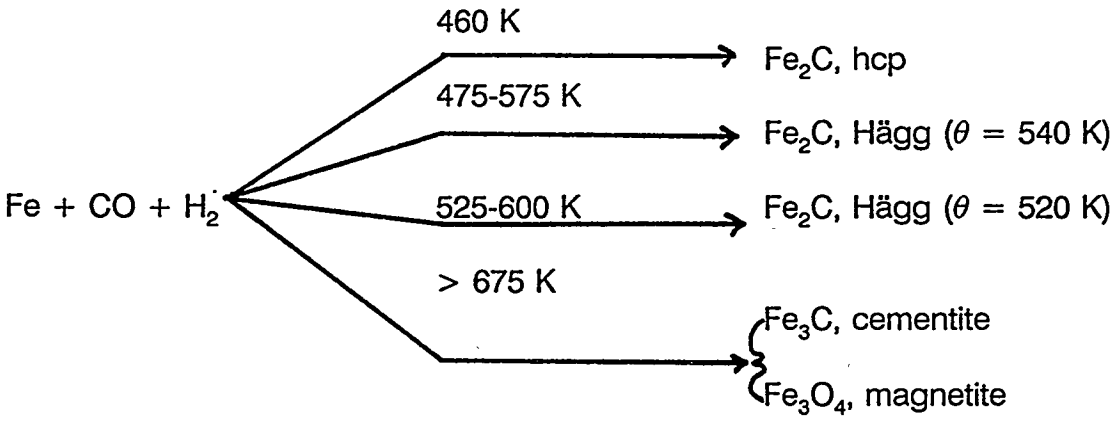
2. a reduced sample is carburized with H_2:CO = 2:1 at 310°C (hourly space velocity 2,500) for six hours.

Considerable work has been done since that time. For example, Sancier et al. (V-7) reports that during carburization of iron, the bulk reaction leads to the formation of different iron carbides which can undergo further solid-phase reactions. Both types of reactions are temperature dependent. Sancier et al. (V-7) summarize the carburization reactions and phase changes as outlined below:

Table V-1

Principal Carburization Reactions of
Iron and Phase Changes (from ref. V-7)

Carburization Reactions



Phase Changes

Fe_2C, hcp ——— 616 K ———→ Fe_2C, Hägg

Fe_2C, Hägg (θ = 540 K) ——— 630 K ———→ Fe_2C, Hägg (θ = 520 K)

Fe_2C + Fe ——— < 770 K ———→ Fe_3C

$3Fe_2C$ ——— 770 K ———→ $2Fe_3C$ + C

Fe_3C ——— 873 K ———→ 3Fe + C

V.2. SUMMARY OF GERMAN WORK PRIOR TO AND DURING WWII

The extreme flexibility of the iron-catalyzed process has the disadvantage of introducing difficulties in reproducibility of catalyst performance, and despite the amount of research work carried out it would appear that no iron-catalyst process developed in Germany had reached the stage where it could be put into operation on the industrial scale and be expected to work as smoothly and efficiently as the cobalt-catalyst process (V-8). A condensation of the work with iron catalysts in Germany to 1945 is taken from reference V-8.

V.2.1. Ruhrchemie AG

This company prepared over 2,000 trial batches of iron catalysts and carried out experiments on a scale varying from 50 ml to 1,000 liters catalyst (one-tenth full scale). Their studies were confined to the **conventional precipitated type of catalyst**, usually containing - in addition to iron - copper, an activator (often CaO) and kieselguhr. They favored **reduction of the catalyst in hydrogen** before use and the use of recirculation of residual gas in the synthesis. They developed a process to operate with this catalyst at 240-260°C and 20 atm.

The characteristics of the process were as follows:

Catalyst. Fe,100:Cu,5:CaO,10:kieselguhr,150, prepared by rapid precipitation from the nitrates with potassium hydroxide at the boiling point, and reduced in dry hydrogen for about 1 hour at 300°C. Bulk density: 0.404.

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

Raw material:	water gas H_2:CO = 1.27:1, inerts = 13.7%
Temperature:	251-257°C
Pressure:	20 atm. (gauge)

Recycle ratio: fresh gas 1:residual gas 2.5
Gas throughput: 98m^3/hr. water gas, space velocity ca. 90/hr.

Results (average figures for 120 days running):

Gas contraction:	52.0%
Yield of liquid and solid hydrocarbons:	103.0 gm/m^3 H_2 + CO
Yield of C_3 and C_4 hydrocarbons:	13.5 gm/m^3 H_2 + CO
Production of C_1 and C_2 hydrocarbons:	11.0%
Production of CO_2:	26.8% of CO converted
Utilization ratio H_2:CO:	1.23:1

Composition of Product:

Naphtha, 60-200°C:	46 wt.%, olefins: 66 vol.%
Oil, 200-320°C:	18 wt.%, olefins: 52 vol.%
Soft wax, 320-460°C:	19 wt.%
Hard wax, > 460°C:	17 Wt.%

Ruhrchemie guaranteed a yield of 140 gm primary products (including C_3 and C_4) per m^3 inert-free water gas by working in two stages and changing the catalyst every 4 months. The catalyst cost 3.7 pfg/kg for total primary products for a catalyst life of 4 months. These figures are higher than the corresponding ones for the cobalt catalyst, due mainly to the cost of the potassium hydroxide and nitric acid used. They could be reduced somewhat by recovery of potassium nitrate from the mother liquor and wash waters.

From the end of 1942 onwards Ruhrchemie concentrated on the development of an iron catalyst which could be used in existing reaction vessels, i.e., one which would operate satisfactorily at 10 atm and at temperatures not greater than 225°C. Their most promising "low-temperature" iron catalyst (discovered after experiments with ceria in place of calcium oxide) was, apart from the kieselguhr content, similar in composition to the earlier high-temperature catalyst. The composition was Fe, 100:Cu,5:CaO,10:kieselguhr,30, prepared by precipitation from the nitrates with

sodium carbonate solution at the boiling point and impregnated, after filtering and washing, with 3% KOH (based on iron content).

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

Reaction Conditions over 5 Months Operation:

Raw material:	water gas
Temperature:	200-220°C
Pressure:	10 atm.
Recirculation ratio:	1 part water gas:2.2 parts residual gas
Gas throughput:	500 liters/hr. (space velocity:100/hr.)

Average Results:	For 1st Month	For 5th Month
Yield of hydrocarbons higher than C_1, gm/m^3 H_2 + CO	121.5	118.3
Methane formed, % CO converted	3.6	4.7
Utilization ratio H_2:CO	1.04:1	1.12:1
Composition of Product:	Wt.%	Wt.%
Naphtha, 60-200°C	16.5	25.1
Oil, 200-320°C	15.9	17.8
Soft wax, 320-460°C	27.9	25.5
Hard wax, > 460°C	39.7	31.6

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

V.2.2. Kaiser Wilhelm Institute (Mülheim)

The characteristic features of the work in this organization were the use of catalysts containing **no carrier or support and consisting only of iron, copper and a little alkali** (potassium salt) and the **pretreatment of the catalyst in CO or gases**

containing CO in preference to reduction in hydrogen. In further contrast to Rührchemie they had paid little attention to developing catalyst specifically adapted to utilizing hydrogen and carbon monoxide in the proportions found in water gas and carried out many experiments using gas with an H_2:CO ratio of 2:3, i.e., the proportions in which the gases react in the presence of the majority of iron catalysts when there is no residual gas recirculation.

The Institute regarded **the pretreatment of the catalyst as being of greater importance than the composition** and the latter was more or less fixed at Fe,100:Cu,1-3:K_2CO_3,0.5-1. It was prepared by rapid precipitation of the nitrates (or preferably a mixture of ferric nitrate, ferrous chloride and cupric nitrate) at the boiling point with potassium carbonate solution, washing free from alkali salts and then adding the required amount of potassium carbonate solution, drying and granulating.

The recommended pretreatment consisted in passing 25 liters/hr. pure CO for each 10 gm Fe for 4 hours at 325°C and at 0.1 atm absolute pressure or passing water gas at 4 liters/hr. per 10 gm Fe for 2 to 3 days at 240-250°C and at atmospheric pressure. This treatment causes **the formation of Fe_3C which is claimed to be the active form of the catalyst.**

The highest conversions were obtained at 20 atm. with synthesis gas of H_2:CO ratio 2:3. Under such conditions an average yield of 120 gm of hydrocarbons higher than methane per m^3 of synthesis gas was maintained for a year using a temperature of 235°C. It was admitted that, owing to carbon deposition when using gas rich in CO, inclined tubes with a free space above the catalyst to allow for expansion had to be employed and that for technical operation it would be preferable to employ water gas.

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

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

V.2.3. IG Farbenindustrie AG

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

V.2.3.a. Fixed-bed, Circulating-gas Process. In this process the "traditional" method of heat dissipation by use of a multiplicity of cooling tubes and surfaces is discarded and the heat of reaction is removed in the gas stream by recirculating 100 volumes of residual gas for every volume of fresh gas introduced, the catalyst being arranged in a shallow, wide bed (e.g., 1.0 mm deep by 1.5 m diameter).

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

Process Conditions:

Synthesis gas:	H_2:CO ca. 1.25:1, S < 0.2 gm/100 cm^3
Temperature:	ca. 325°C
Pressure:	20 atm.

Contact time:	0.5-1 sec.
Recycle ratio:	100:1

Products:	Wt.%
Ethylene + C_3 + C_4:	30
Naphtha, < 200°C:	48 (7% alcohols, olefins 70%)
Gas oil:	14 (4% alcohols)
Wax:	1
Alcohols from reaction water:	7 (mainly C_2)

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

The crude naphtha had an octane number of 68-70. The process had been operated successfully over a period of 10 months on a scale of 5 liters catalyst but larger-scale experiments had not been so successful, due either to turbulence or channeling, both of which lead to local overheating of the catalyst.

V.2.3.b. The Foam Process. The object of this process was to produce olefins boiling in the gas oil range for use in chemical synthesis. The catalyst was prepared by pasting carbonyl iron with potassium carbonate or borate, drying and reducing in hydrogen at 350-450°C. The reduced catalyst was ground to a fine powder in a ball mill in the presence of gas oil, and the reaction was carried out by forcing water gas through a ceramic plate at the base of a cylindrical vessel containing a suspension of the catalyst in a high-boiling fraction of synthetic oil (i.e., a type of slurry reactor).

Process Conditions:

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

Products:	Wt.%
C_3 + C_4:	10
Naphtha, < 200°C:	40-50 (70% olefins)

Oil, 200-350°C:	30 (40-50% olefins)
Wax:	20-25

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

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

V.2.3.c. Conventional Tubular Reactor Process. This process utilized the normal type of tubular reactor with water cooling, but employed the sintered type of catalyst favored by IG. The catalyst was **prepared by mixing iron oxide with 5-25% MgO or $MgCO_3$ and 1-2% potassium carbonate or borate, pelleting and then sintering by heating to 850°C in nitrogen, cooling and then reducing in hydrogen at 350-450°C.**

Process Conditions:

Synthesis gas:	H_2:CO = 1.25:1 to 0.8:1
Temperature:	230-250°C
Pressure:	20 atm.

Products:

$C_3 + C_4$:	10% (olefins 70%)
Naphtha, < 200°:C	30-50% (olefins 70%, oxygen 4-6%)
Oil, 200-350°C:	25-35% (olefins 40-50%, oxygen 3-5%)
Wax > 350°C:	15-25%
Output of above products:	350-450 kg/day per m^3 catalyst space
Methane Production:	10 kg/100 kg "useful" products

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

V.2.3.d. Fixed Bed, Circulating Oil Process. In this process the same catalyst as that employed in the preceding process (tubular reactor process) was used but in place of external water-cooling, the heat of reaction was removed by circulating oil through the catalyst bed.

Process Conditions:

Synthesis gas:	H_2:CO = 0.82:1
Temperature:	260-300°C in Stage I, 280-330°C in Stage II
Pressure:	20-25 atm.
Gas throughput:	Controlled to give 20-25 gm/hr. products per liter catalyst
Conversion:	ca. 150 gm useful products/m^3 H_2 + CO

Products:	Wt.%
$C_3 + C_4$:	16 (85% olefins)
Naphtha, < 200°C	40 (50% olefins)
Oil:	20 (25% olefins)
Wax:	20
Alcohols ($C_1 + C_2$):	4

The naphtha contained 1% oxygen and had a research octane number of 62-65. The process had been operated for a long period in a pilot plant with an output of 8-10 ton/month.

V.2.3.e. The "Synol" Process. **This process was designed for the production of straight-chain primary alcohols for use as chemical intermediates. The catalyst was prepared by melting iron in a blast of oxygen and incorporating aluminum nitrate and potassium nitrate in the melt so that the finished product contained 2% Al_2O_3 and 1% K_2O based on iron content. It was identical with that used by the IG for ammonia synthesis and was reduced in hydrogen at 450°C before use.**

Process Conditions:

Synthesis gas:	H_2:CO = 0.75:1
Temperature:	185 rising to 200 or 225°C after 9 months
Pressure:	18-20 atm.
Space velocity:	100-150
Recycle ratio:	50:1

By using two stages in series a yield of 155-165 gm of liquid products per m^3 H_2 + CO was obtained.

Products: Fraction	Wt.% of total	Wt.% alcohols	Wt.% paraffins	Wt.% olefins
Up to 150°C	70	20	40	40
150-200°C		70	15	15
200-300°C	30	50	20	30
> 300°C		30	42	28

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

V.2.4. Lurgi Gesellschaft für Wärmetechnik

The best iron catalyst developed by this company in their Frankfurt-am-Main laboratories was stated to have the composition Fe,100:Cu,25:Al_2O_3,9:K_2O,-2:kieselguhr,30. **It was prepared by precipitation from the nitrates with sodium carbonate solution at the boiling point, filtering and washing the cake and then adding the required amount of alkali as K_2CO_3. Reduction in hydrogen at 250-350°C for 1-4 hours was carried out before use.** The catalyst was designed for use in conventional-type reaction vessels in a two-stage process using water gas as raw material and employing a 2.5:1 recycle in Stage I.

Process Conditions:

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

Products:	Wt.%
Naphtha	20 (olefins 60%)
Oil, 200-320°C	20 (olefins 45%)
Soft wax, 320-460°C	15
Hard wax, > 460°C	45

V.2.5. Rheinpreussen

This company had carried out laboratory research on precipitated iron catalysts containing copper and alkali with magnesia as activator and dolomite or kieselguhr as support. **As a result of studies of carbide formation they had concluded (like the KWI) that pretreatment of the catalyst with a low partial pressure of CO was preferable to reduction in hydrogen.** They found that a recycle ratio of 10:1 gave optimum results and claimed yields as high as 150 gm C_2 and higher hydrocarbons per m^3 inert-free gas for single-stage operation at 10 atm. and 200-220°C. One sample of catalyst had been maintained in operation for 3 1/2 years and was still giving a yield of 130 gm C_2 and higher hydrocarbons per m^3 at the end of that period.

This organization appears to be alone in having achieved considerable success in the development of an iron catalyst suitable for atmospheric pressure operation. Thus, for example, a catalyst of composition Fe,100:Cu,10:Mg,20:kieselguhr,50:K_2CO_3,2, gave a yield of 135 gm C_2 and higher hydrocarbons per m^3 (H_2 + CO) in one stage at atmospheric pressure and 200-220°C using synthesis gas (H_2:CO = 2:1) and recirculating 10 parts of dried CO_2-free residual gas to each part of fresh gas introduced.

V.2.6. Brabag

Comparatively little is known of this company's work on iron catalysts. One preparation containing 5-6% K_2CO_3 gave an average yield of 146 gm C_2 and higher

hydrocarbons per m^3 (H_2 + CO) at 246°C over a period of 3 months. The products contained 70-80% of olefins and the octane number (research) of the naphtha-fraction (38-160°C) was claimed to be 82.

V.2.7. The "Reichsamt" Comparative Experiments

The trials of six different iron catalysts were carried out in 5-liter catalyst vessels at the Ruhland-Schwarzheide works of Brabag, and started in September, 1943. The conditions to be employed were as follows:

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

The experimental data and results are summarized in Table V-2.

Table V-2
Data for Reichsamt Tests of Six Iron Catalysts
Pressure: 10 atm., Raw material: water gas containing 12% inerts
Method of operation: single-stage without recirculation
Period of test: 90 days

Reaction Vessel No.	1	2	3	4	5	6
Organization Supplying Catalyst	KWI	Lurgi	Brabag	IG	Ruhrchemie	Rheinpreussen
Catalyst volume - liters	4.8	4.8	4.8	4.8	4.8	4.8
Catalyst weight - kg	4.9	3.79	6.08	10.9	2.1	3.28
Reaction temperature, °C	195-224	188-220	219-225	163-220	186-222	190-224
Space velocity, vols gas/vol cat. space/hr.	108.7	106.9	110.7	115.0	103.8	104.0
Gas contraction, %	42.7	39.1	36.4	38.5	33.0	39.2
H_2 + CO converted, %	69.3	64.8	58.2	63.1	54.2	57.2
Yield of hydrocarbons, excluding CH_4, gm/m^3 water gas	112.2	112.2	102.7	105.8	92.8	94.2
Yield of CH_4, gm/m^3 water gas	9.9	6.4	3.0	7.8	5.5	7.9
Yield of oxygen in primary products, gm/m^3 water gas	3.1	5.9	2.7	3.5	4.8	1.9
H_2 utilization, moles per mole of CO	0.80	0.66	0.69	0.74	0.72	1.07
Composition of Total Products:						
Gases C_1 and C_2, wt.%	16.6	10.8	8.4	16.8	13.6	17.1
Gases C_3 and C_4, wt.%	19.9	12.3	9.8	18.1	14.3	21.5
Naphtha, C_5-C_{10}, wt.%	25.1	19.5	17.9	25.7	22.3	29.8
Diesel oil, C_{11}-C_{18}, wt.%	14.0	13.1	16.4	11.5	12.7	13.7
Soft wax, 320-450°C, wt.%	7.9	8.2	12.6	6.1	7.1	6.3
Hard wax, >450°C	10.3	27.0	30.8	14.8	18.7	6.3
Low-boiling alcohols	6.2	9.1	4.1	7.0	11.3	5.3
	100.0	100.0	100.0	100.0	100.0	100.0
Total alcohols, wt.%	7.0	14.4	9.5	10.7	15.8	7.5
Total esters, wt.%	1.1	8.0	2.7	1.7	2.6	0.3
Total olefins, wt.%	25.9	30.4	34.2	39.1	26.1	29.7

Catalyst Data

KWI - Composition - Fe,100:Cu,1:K_2CO_3,1 by precipitation from nitrates. Reduced in synthesis gas H_2:CO = 2:1 at 325°C and 0.1 atm. (absolute) for 24 hours.
Lurgi - Composition - Fe,100:Cu,10:SiO_2,30:K_2O,2. Reduced in hydrogen at 250-250°C.
Brabag - Composition (by Ruhrchemie analysis) - Fe,100:Cu,20:Zn,20:K_2CO_3,1. Pretreated in water gas at 235-240°C for 48 hours.
IG - A sintered iron catalyst containing Al_2O_3 and K_2O and using calcium fluoride as support.
Rührchemie - Composition - Fe,100:Cu,5:CeO_2,10:kieselguhr,50 by precipitation from nitrates. Reduced in hydrogen at 300°C.
Rheinpreussen - Composition - Fe,100:Cu,5:$CaCO_3$,100:K_2CO_3,0.5-1.0. Reduced in water gas at 240-250°C, atmospheric pressure.

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

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

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

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

V.2.8. Work of Fischer, Tropsch and Pichler

Pichler and Merkel summarize the work of Fischer, Tropsch and Pichler (V-9). Early work by Fischer and Tropsch used alkalized iron filings at 100 atm pressure and temperatures between 350 and 450°, they obtained a mixture of oxygenated compounds (Synthol process). For synthesis at atmospheric pressure, Fischer and Tropsch used iron catalysts prepared, for example, by decomposition of iron nitrate and these were further activated by the addition of such substances as copper,

manganese, or alkali. For medium pressure synthesis, Fischer and Pichler used precipitated iron catalysts that were pretreated with carbon monoxide-rich gas at atmospheric or lower pressure, and then operated between 10 and 30 atmospheres. An especially active catalyst, for instance, was formed by pretreating with carbon monoxide at 0.1 atmosphere and 325°C, and subsequently operating the synthesis with water gas at 15 atm. and 210° to 230°.

Fischer and Pichler (V-9) also utilized hydrogen reduction as a part of their pretreatment. The activity of iron catalysts reduced with hydrogen at different temperatures to Fe_3O_4 or to metallic iron was no greater than that of untreated iron catalysts when used in the hydrocarbon synthesis at atmospheric or at higher pressures.

If an iron catalyst was used at pressures of 10 to 30 atmospheres without pretreatment, satisfactory reactivity of CO/H_2 mixtures would be obtained only at high temperatures, that is, 280 to 300°C and at these temperatures the fraction of gaseous hydrocarbons were too large (V-9). **However, when these iron catalysts were treated with carbon monoxide rich gas (for example, pure CO or water gas) at pressures lower than those used for the synthesis (atmospheric pressure or preferably lower), the high activity of the catalysts resulted in satisfactory synthesis of chiefly liquid and solid aliphatic hydrocarbons at temperatures between 220 and 230°C.** Thus, carburization made it possible to lower the synthesis temperature by 60 to 80°C. The increased activity persisted even after the catalyst had been used over a period of months.

These authors (V-9) summarize with the statement: "It has already been stated that treatment of iron catalysts with carbon monoxide before synthesis is desirable."

"Free carbon," that is, carbon that remains following acid decomposition of the carbided form of the catalyst, is always present (V-3). The amount of this carbon appears to depend upon the length of exposure to a CO rich gas (Figure V-2). It also

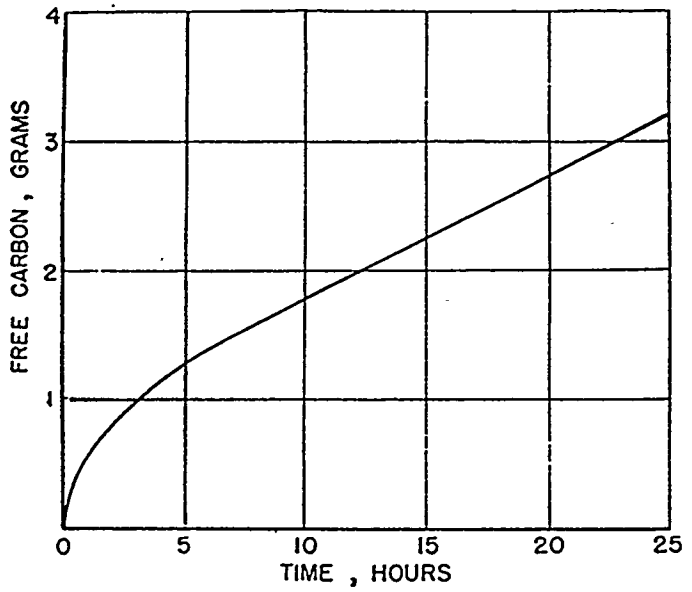


Figure V-2. Free carbon deposition of alkalized-iron catalyst at 325°C and 0.1 atmosphere, 40 liters of CO per hour, 10 grams of Fe (from ref. V-9).

appears that the long-term activity of the catalyst depends upon the amount of the free carbon; the higher (within reason) the free carbon the longer the catalyst retains the activity (Table V-3.)

Table V-3

Effect of Catalyst Activity on Formation of Free Carbon

(40 L CO/10 g Fe for 2.5 hr. at 325°C and 0.1 atm CO; from ref. V-9)

Catalyst	Free Carbon (grams)	Period catalyst showed full activity, days
Z 7	0.81	6-10
Z 4	1.07	6-10
Z 3	1.75	35 +

The carburization using CO continues for a long period of time. The amount of CO_2 in the exit gas is illustrated in Figure V-3. The authors state that the first, rapid

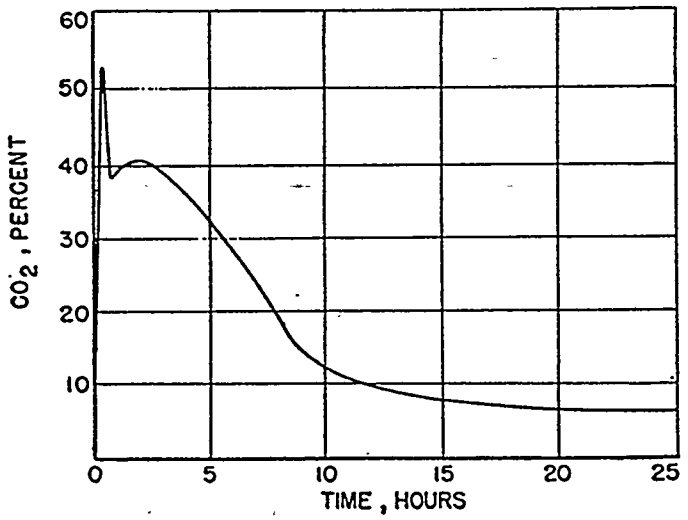


Figure V-3. Carbon dioxide content of tail gas during carburization of an alkalized-iron catalyst at 325°C and 0.1 atmosphere, 4 liters of CO per hour (from ref. V-3).

formation of CO_2 is due to the reduction of Fe_2O_3 to Fe_3O_4. The authors report that the second peak is due to the reduction of Fe_3O_4 to Fe and to the beginning of

carbide formation. The later stages of the formation of CO_2 is due solely to the reaction:

$$2\,CO \rightarrow C + CO_2 \qquad [V\text{-}4]$$

These authors cite evidence to support the advantage of carburization with CO at low pressures (V-3). The durability of the catalyst is illustrated by comparing a catalyst that was carburized at 2 mm Hg and maintained a maximum yield after more than 3 weeks to one carburized at 15 atm. which was completely inactive after 3 weeks. The durability of the catalyst also depends upon the temperature that the catalyst is carbided at the low pressure. The dependence of the length of time that the CO conversion remains above 91% and the amount of free carbon in the catalyst is represented in Figure V-4. It was reported that the large amount of carbide present

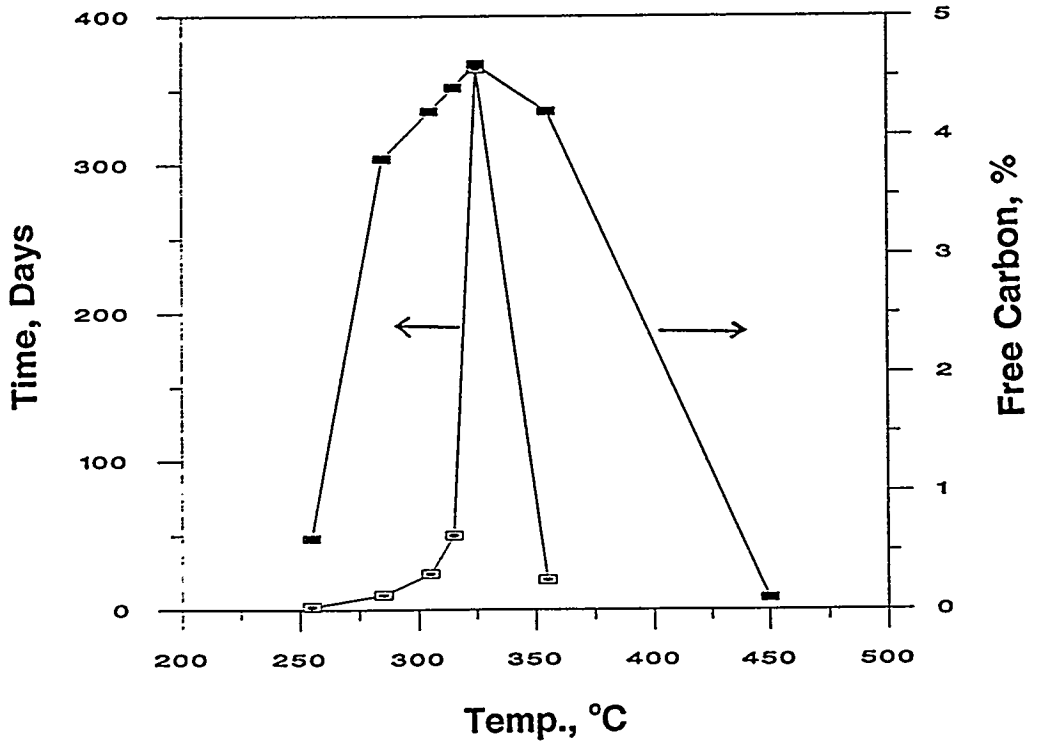


Figure V-4. The deposition of free carbon (■) and the number of days with a CO conversion greater than 90% (□) as a function of the carbiding temperature (from ref. V-3).

after pretreatment decreased during the first days of operation to 2-4 g C/100 g Fe and that there was a corresponding increase in the oxygen content to 1-2 g O/100 g Fe. The catalyst maintained this "equilibrium" carbide-oxide composition for months.

2.9. Kölbel

Kölbel and Ralek (V-10) describe the results of extensive FT studies in laboratory and demonstration plants operating in the slurry phase. While there have been questions concerning differences between the German work and that reported subsequently (see, for example, the discussion following reference V-11, and the claims of the operation of the demonstration plant, the reports are substantial. The authors reported that it was an advantage for the catalyst particles to break up during the syntheses as a result of carbide formation, and therefore support-free catalysts were preferable. These catalysts make it possible to use the highest concentration of iron in suspension, with the optimum concentration reported to be about 10 wt%. Higher concentrations of catalyst slurry up to about 20 wt% can be used but they increase the viscosity of the suspension, and thus decrease the interfacial area introducing mass transfer effects.

The precipitated catalysts were obtained from iron(III) nitrate solutions or mixtures of nitrate solutions containing 80% iron(III) and 20% iron(II) (V-12,V-13). The authors reported that solutions of iron(II) cannot yield active catalysts because the iron in the oxide has to be present either as α- or γ-Fe_2O_3. Either during calcination or activation, the authors report that the indispensable Fe_3O_4 phase is produced. The authors report that the presence of impurities contained in the nitric acid used to prepare iron(III) nitrate (e.g., Mn, SiO_2, C and even catalyst poisons like sulfur and phosphorous) did not reduce the activity of the finished catalyst. In fact, the presence