HYDROCARBON SYNTHESIS WITH IRON CATALYSTS

By Dr. Roelen

The use of iron as a catalyst for the hydrogenation of carbon monoxide to higher hydrocarbons dates far back. The Badische Anilin und Sodafabrik has published already in 1913 information on the production of higher hydrocarbons from carbon monoxide under pressure using iron catalysts.

Franz Fischer and co-workers have carried out extensive experiments in that field at a later date, between 1921 and 1924, in the KwI in Muelheim-Ruhr. We may consider the characteristics of this experimental period to consist in the activation of iron by means of alkalies. The methods of preparation of catalysts at that time were still very imperfect and the activity was relatively low. Iron was used in a compact form, e.g. as iron filings coated with potassium carbonate. Such masses were naturally but little active. Work had to be done under such physical conditions which forced conversion to the limit, namely at high pressures and high temperatures, e.g. at 150 atm gauge and 400-450°C. Liquid products were then obtained, but no hydrocarbons, namely only oxygen-containing substances. This mixture was called synthol. It is of interest

to know in this connection, that the synthol tests were not fur-
ther continued, because of the impossibility of obtaining cata-
lysts of long life. The masses became hard and plugged up after
a short time and could be removed from the reaction space only
with great difficulty.

We learned at that time to improve the catalyst produc-
tion by finer subdivision of the active metal, and the tempera-
ture and pressure could be then lowered. The first production
of higher hydrocarbons at atmospheric pressure was successfully
done in 1925 using catalysts prepared by mechanical mixing of
iron oxide and zinc oxide. The reaction temperature still was
at 365-380°C, i.e. still relatively high.

It had been recognized already in 1925, that cobalt was
also capable of forming higher hydrocarbons. The tests with
cobalt were not, however, at first continued, in part because
they were not very successful, in part also because of the high
cost of cobalt. Thus, during the first four years of the develop-
ment of gasoline synthesis work was done almost exclusively with
iron catalysts. At that time chiefly decomposition catalysts were
made obtained by roasting of nitrate mixtures. The yields obtained
with that type of catalyst were rather small. Even in 1929 the
maximum yield did not exceed 11 mls of liquid products per cbm
water gas. The revaluation of the English pound sterling to one-
half its former value happened in that year. This reduced the
purchase cost of cobalt to about one-half. The experiments with
the cobalt catalysts were started afresh. The introduction to

cobalt of the improved production methods already developed for
iron resulted immediately in appreciable progress, and two years
later a yield of 100 g/cbm could be reached. Since that time,
i.e. since 1930, the development went almost exclusively by way
of the cobalt catalyst, and the iron catalysts have not been
studied to any extent for ten years.

A particular inducement to start anew the tests with
iron has been produced some time ago after the development of
the cobalt catalyst had reached a certain limit. Experiments
with iron catalysts were taken up in Germany again in at least
six different places, independently from each other.

Franz Fischer has communicated in a closed meeting of
the KWI his new experimental results with the iron catalysts. A
second such meeting has taken place last Tuesday, September 10,
1940. The principal points from H. Pichler's report are here
repeated:

1) Catalysts were used containing only iron or at most
also alkalies, and formed by precipitation with soda or ammonia.

2) "Forming" is required prior to starting. This con-
sists in a pretreatment with carbon monoxide or carbon monoxide-
rich gases at higher temperatures but lower pressures than the
synthesis pressure.

3) The preferred synthesis conditions are 15 atms,
220-250°C, CO-rich gas.

4) The yields obtained were 5-50% paraffins or 40-80%
gasoline. The stabilized and washed gasoline contained 64%

olefines, 90% came over -145°C and had an octane number of 61.

5) It was particularly important, that the volume of the catalyst mass increased during operations, and that the catalysts had a tendency for deposition of elementary carbon. As a result these catalysts could best be used in a horizontal layer. With a vertical layer, difficulties arose in the gas passing through the catalysts and much effort had to be used for overcoming them, and the investigations in that field are still in progress.

The patent applications of the I.G. between 1935 and 1937 have, in the meantime, become known and included a new type of iron catalyst obtained by sintering of mixtures of finely divided iron with other substances. This type of sintered catalysts is naturally considerably less active than precipitation catalysts and require relatively high reaction temperatures, e.g. 320-380°C.

The Lurgi Company, Frankfort/Main has developed an iron precipitation catalyst which operates at about 250°C with rather good results.

Synthesis experiments with iron catalysts have also been carried out in the meantime in the laboratories of the Brabag Company in Schwarzheide. They also obtained good results using precipitation iron catalysts.

Dr. Kölbel has already reported on the results of the experiments in Rheinpreussen.

As far as our experiments in Holten are concerned, we have not limited ourselves to prepare a single catalyst which would give

optimum results but have tried rather to apply the experience gained in the meantime with cobalt to carry out the work on a broad basis. As a result we are now in a position to produce individual catalysts for a great variety of purposes, as I will show you later on a few examples.

We have investigated the preparation of the catalysts by roasting of nitrates and particularly the preparation of the precipitation catalysts of the most diversified kind. Without giving details on the preparation of catalysts proper, we may say the following about the general experience with our iron catalysts. We may consider the low hydrogenation property of iron as being in several respects the principal difference from cobalt. The liquefaction is throughout more favorable than with the cobalt, in spite of the fact that all iron catalysts known heretofore operated at higher temperatures than cobalt. In addition, the saturation state of the liquid products is considerably lower, permitting the production of large yields of the valuable olefines. The lower tendency for methane formation in comparison with cobalt permitted operations with a much wider range of synthesis conditions, without causing either excessive gasification or too low conversion. This offers greater possibilities to affect the course of the synthesis by changing operating conditions, and in particular to change the boiling point range.

Iron differs appreciably from cobalt also in one other respect, namely with respect to the proportion of carbon monoxide and hydrogen used up. This proportion of consumption of CO and H_2

is not constant with cobalt and may be changed with the composition of the gas or by pressure. However, these changes of the gas or of the pressure are very slight with cobalt and permit the variation between 1 $CO:1.9-2.1$ H_2. On the other hand, with iron the proportion may be varied much more depending on the mixture, the form of the catalyst and the experimental conditions, producing the greatest variety of consumption proportion.

　　　　We have investigated this in detail and can today indicate to a certain extent the proportion of carbon monoxide to hydrogen between the limits $0.6-1.4$ $H_2:1$ CO, which can be set at will by proper choice of the iron catalyst. We can in particular prepare such iron catalysts which consume carbon monoxide and hydrogen in the exact proportion in which they exist in the water gas. We can in this way overcome the difficulties of having to produce gases with appreciably more carbon monoxide than in the water gas.

　　　　It has been necessary so far to use a composition of a gas with cobalt catalysts which corresponded to the definite consumption proportion. This required the preparation of a special synthesis gas. Dr. Kölbel has just now stated that the gas composition had to be adjusted to the catalyst. We can, on the other hand, produce iron catalysts of such composition that it will be suitable with the gas most easily produced, the water gas.

　　　　You might state that carbon monoxide-rich gases may be necessary for the production of definite products, such as a high olefine or high paraffin content. Such is, however, not the case.

We shall show below the possibility of production of any desired products from water gas.

Changing over to water gas introduces a further advantage. The carbon monoxide-rich gases favor the deposition of elementary carbon, which may lead to notable difficulties in operations. We have completely overcome this danger by using our new catalysts.

The iron catalysts developed by us can be started in a variety of ways. We may subject them to a pretreatment at atmospheric pressure at temperatures reached in the synthesis and using water gas. It is remarkable that water gas may also be replaced by other gases, such as nitrogen, carbon dioxide, or even air. We have found that starting with water gas at high pressure is disadvantageous and in many cases results in failures. Unlike Fischer and his collaborators we have had good results with reduction with hydrogen, which was much easier with our iron catalysts than with the usual cobalt catalysts. Such iron catalysts can be reduced and made ready for operations in the reactors, without any loss of time for "forming", as is also the case with cobalt catalysts. Fischer has furthermore suggested to carry out the pretreatment of the catalysts with carbon monoxide in vacuum. This, however, offers no particular advantages nor experience.

We have found that with iron catalysts, predictions of their activity at higher pressures could not be made from behavior at atmospheric pressure. One is therefore forced to carry out all middle pressure catalyst tests at elevated temperatures. Pressure

resisting experimental reactors are not as readily obtained as for atmospheric pressure reactors, and we had to use short tests of the different catalysts instead of the long duration tests. Nevertheless, we may consider the life of our iron catalyst to be at least as great as that of the present cobalt catalyst, basing it on semi-technical tests. We have succeeded in raising the activity of the iron catalysts to such an extent, that the reaction temperature could be used close to that used with cobalt catalysts, namely 220-230°C. These temperatures are still too high to permit the use of iron catalysts in the large industrial reactors at present available. We therefore make the efforts to further improve the catalyst preparation to permit a further lowering of the reaction temperature. We also are working on a new type of reactor construction and the practical results obtained with them will be presently reported.

We have carried out our pilot plant tests in pressure water cooled tubular reactors of known construction, e.g. in reactors with a gas thruput of 12 cbm/h. We duplicated the best results of our laboratory tests in a pilot plant - produced iron catalysts making long term tests. Our pilot plant tests have shown that the iron catalysts differ favorably with respect to hardness of the particles from the cobalt catalysts. As a result, our iron catalysts have a very high abrasion resistance. One sample, which has been used for two months in the pilot plant reactor, showed no carbon deposition nor increase in volume. The emptying of the reactors offers no difficulties.

It is well known that all products of the catalytic hydrogenation of carbon monoxide contain more or less of oxygen-containing compounds, and the more the higher the reaction pressure. The middle pressure products obtained with the iron catalysts contained correspondingly variable amounts of oxygen-containing materials, depending upon operating conditions and the catalysts used. We have even found that relatively large amounts of oxygen-containing primary products can be readily produced. This direction of the synthesis appears, however, in many respects less promising:

1) The oxygen-containing products are non-uniform, and consist by no means of alcohols only.

2) The lower molecular weights are mostly present, rather than the more valuable higher molecular weight compounds.

3) The oxygen-containing constituents cannot be separated by available means from the hydrocarbons.

4) We have found in the meantime other ways to produce oxygen-containing products in the pure state, such as alcohols, acids, esters, ketones, aldehydes, etc.

I will now tell you the numerical data obtained in our experiments, starting with the dependence of the course of the synthesis from the catalysts, then from the operating conditions and finally the summarized results.

Table 1 shows that we can produce with this catalyst either more gasoline or more paraffin (20-58% gasoline or 50-3% paraffin) with the same operating conditions.

The maintenance of the most favorable metal concentration has been of prime importance for the activity of the cobalt catalysts. The large number of tests performed have caused the adoption of the lower cobalt mixtures. This is the reason why, unlike the KWI and Rheinpreussen, we have not yet reached the conclusion that the question of the addition of carriers to iron catalysts has been definitely solved in favor of the carrier-free catalysts. We have instead studied carefully the proportions for iron.

Table 2 shows an illustration of the changes in the course of synthesis with the metal concentration. Higher boiling products are obtained with iron with increasing metal concentration, other conditions being left the same and vice versa. The preparation of catalysts involves a number of operations which may be changed. Table 3 shows changes in the course of synthesis produced by varying the operations during the catalyst production, while retaining the composition of the mass. This measure alone has been found sufficient to affect appreciably the liquefaction and the boiling point range.

Table 4 shows the same thing for a second variation of a single operation in the preparation of the catalysts of the same composition. This again permitted changing the boiling point curve as well as degree of saturation (10-25% gasol, 16-45% gasoline, 35-66% paraffin, 54-75% olefines).

Table 5 shows the possibility of affecting the boiling points and degrees of saturation by a third variation in the

preparation of the catalysts of the same composition (16-52% gasoline or 66-22% paraffin).

We have verified the fact that such variations in the preparation can be equally successfully carried out on a pilot plant scale, as can be seen from Table 6.

The subsequent tables show the possibilities of changing the course of the synthesis with the same catalysts by using different synthesis conditions. Table 7 shows the effect of increase in pressure. In agreement with the results obtained elsewhere, the conversion at atmospheric pressure was considerably less than at higher pressure. We were forced to operate at the 75% CO conversion at an elevated pressure to obtain the same yields as are obtained at atmospheric pressure with a 95% conversion of CO. Obviously under such conditions the liquefaction is correspondingly poorer. For the same CO conversion, the yield increased with increasing pressure up to 10 atms gauge, and was no longer appreciably higher at 20 atms gauge. The boiling point curve changes in the well known way in producing less gasoline and more paraffin with increased pressure. The degree of saturation is not appreciably affected by increasing the pressure.

Table 8 shows the effect of the method of operation from the composition of the gas. We mean specifically under operating conditions the details of gas supply, as e.g. the flow velocity, etc. The more carbon monoxide and the less hydrogen is present in the tail gas, the less gasoline and the more paraffin is obtained. The amount of unsaturated hydrocarbons increases simultaneously with increasing carbon monoxide content.

We have found that with the iron catalyst the dilution of gases or increasing the flow velocity operated in the same way, namely by increasing the gasoline yield and the olefine content, while the paraffin formation was lowered, as can be seen in Table 9.

The individual examples cited above show that the boiling points and degree of saturation of the liquid products can be affected by a whole number of different measures. Were we to utilize all these possibilities simultaneously, i.e. were we to select the catalyst and the method of operation for the optimum conditions, one could easily get up the desired highest gasoline or paraffin yield or else the highest yields in unsaturated hydrocarbons. Table 10 shows a few examples. The first method of operation produced 81% gasoline and 6% paraffin. The paraffin contained 70% sulfuric acid-solubles and had an octane number of 69, or when leaded - 81 (boiling -200°C). We obtained only 14% gasoline and 64% paraffin yield in the third method of operation.

An improvement in the octane number of the primary product has heretofore been possible exclusively by increasing the proportion of unsaturated hydrocarbons. We know, however that there exists a further possibility by producing a strong branching of hydrocarbons in the primary products. We have made attempts to work in this direction, and have developed special catalysts for this purpose. The second column of Table 10 shows the results with such a catalyst (D). The olefine content of the gasoline

is lower than in the preceeding one but its octane number is appreciably higher, namely 72 (b.p. -200°C). This shows that we have been successful in increasing the proportion of the iso hydrocarbons, as has also been confirmed by a boiling point analysis of the precision distillation fractions.

Table 11 shows numerical examples on the consumption proportion of $CO:H_2$ already discussed above. It may be seen that with seven catalysts of the same composition B, but prepared somewhat differently, the consumption proportion can be changed in relatively small steps over a wide range, keeping other synthesis conditions unchanged. A simultaneous change of the synthesis conditions permitted still further changing of the consumption proportion. A comparison shows further that with increasing carbon monoxide consumption the proportion of the unsaturated hydrocarbons increases. Table 11 shows further that the maximum paraffin yield is obtained when the carbon monoxide hydrogen proportion in the synthesis gas was the same as in the off-gas.

Table 12 shows a pilot plant test, namely the paraffin synthesis from water gas, with all the important data. The low methane formation of only 7% with a yield of 145 g/ncbm of the active gas is worthy of notice. The paraffin yield amounted to 64%.

Table 13 gives juxtaposition of the most favorable individual results so far obtained with the iron and the cobalt catalysts. They show that the iron catalysts do not merely reach the yields obtained with the cobalt catalysts, but even exceed them.

It must, in that connection, be considered that the development of the iron catalyst is by no means concluded, and is still being continued. Further improvements can therefore be anticipated with certainty.

In the discussions which followed, Kölbel has stated that his catalysts were less sensitive to sulfur poisoning but had no numerical data at that time to substantiate his opinion.

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Table 1: Changing the Course of the Synthesis
          by Changing the Catalysts

Fundamentally different methods of preparation and
composition. The same synthesis conditions: 20 atm
gauge, water gas, 245°C, operating method I.

Boiling Point Distribution in Percent by Weight of the
Liquid Products:

Catalysts	Gasoline -200°C	Heavy Oil 200-320°C	Soft Paraffin 320-460°C	Hard Paraffin 460°C
.	58.5	24	14	3.5
B	20.5	13	16.5	50

Table 2: Changing the Course of the Synthesis
          by Changing the Metal Concentration

Catalyst B, water gas, 20 atm gauge, operation I.

Metal Concentration	High	Middle	Low
CO conversion	80	75	75
Yield, g/ncbm of active gas	143	140	115
Gasol, % of the yield	10	17	24
Boiling range:			
Gasoline, % by weight of liquid products	16	27	26
Oil, % by weight of liquid products	18	17	21
Paraffin, % by weight of liquid products	66	56	53
Olefines: % by volume			
in gasoline	64	65	72
in oil	56	54	69

Table 3:   Changing the Course of Synthesis by
           Changing the Preparation of the
                  Catalyst, Variation I

20 atm gauge, water gas, operation I, the same catalyst.
   composition.

Catalysts	B 1	B 2	B 3
Temperature	220	230	240
% CO conversion	75	77	76
% CO in CH₄	14	7	6
% CO in CO₂	35	27	25
Gasol, g/ncbm	23	11	13
Liquid products, g/ncbm	85	130	127
Boiling range:			
% gasoline by wt.	45	16	22
% oil " "	20	18	22
% paraffin " "	35	66	56
Olefines: % by vol.			
in gasoline	69	64	63
in oil	63	56	55

Table 4:   Changing the Course of Synthesis
           (Variations in Catalyst Preparation;
                  Variation II)

20 atm gauge, water gas, operation I, the same catalyst composition.

Catalysts	B 4	B 5	B 6	B 7	B 8
CO conversion	80	75	75	80	80
Gasol, % by wt. of yield	10	16	25	25	20
B.p. range:					
Gasoline, % of liquid products	16	22	33	45	25
Oil, % of liquid products	18	22	23	20	20
Paraffin, % of liquid products	66	56	44	35	55
Olefines: % by vol.					
in gasoline	64	63	65	69	79
in oil	56	55	54	63	75

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Table 5: Changing the Course of the Synthesis
          by Changing the Method of Preparation
               of Catalysts: III Variation

20 atm gauge, water gas, operation I, same composition
  of catalysts.

Catalysts	B 9	B 10	B 11
CO conversion	75	75	80
B.p. range:			
Gasoline, % by wt.	52	45	16
Oil, % by wt.	26	28	18
Paraffin, % by wt.	22	27	66
Olefines: % by vol.			
in gasoline	52	54	64
in oil	46	48	56

Table 6: Variation IV in the Preparation of the
              Catalysts, Pilot Plant

20 atm gauge, water gas, operation I, the same catalyst
  composition.

Catalysts	B 12	B 13
CO conversion	75	75
B.p. range:		
Gasoline, % by wt.	23	17
Oil, % by wt.	16	16
Paraffin, % by wt.	61	67
Olefines:		
% by vol. in gasoline	58	79
% by vol. in oil	49	81

Table 7: Changing of the Course of the Synthesis
                    by Pressure

Water gas, same catalyst, same method of operation.

Pressure, atm gauge	atm Pressure	3	5	10	20
CO conversion	95	75	70	75	75
Yield, g/cbm	90	98	86	118	120
B.p. range:					
% by wt. of gasoline	57	32	30	25	22
" " " " oil	24	30	25	20	22
" " " " paraffin	19	38	45	55	56
Olefines:					
" by vol. in gasoline	68	64	63	62	63
" " " " oil	41	48	49	47	46

Table 8: Changing the Course of Synthesis
          by Altering Method of Operation,
                    Valiant I

20 atm gauge, 245°C, the same catalyst, operating pro-
   cedure and composition vary.

| Operating Procedure | I | | | II | |
	Synthesis Gas	Water Gas	CO-Rich Gas	Water Gas	CO-Rich Gas
% of CO in gas	26.3	38.0	50.9	38.0	50.9
% H₂	52.6	48.9	38.1	48.9	38.1
CO conversion	70	70	60	75	62
B.p. range:					
% by wt. of gasoline	38	25	20	43	20
" " " " oil	20	24	30	20	13
" " " " paraffin	42	51	50	37	67
Olefines:					
% by vol. in gasoline	77	79	86	65	80
" " " " oil	68	76	82	56	74

Table 9:   Changes in Course of Synthesis by Changing
the Operating Procedure to Variation

20 atms, CO-rich gas with 51% CO, 38% H_3, 245-250°,
same catalyst.

Gas Dilution) Increasing Velocity of Flow)				
Yield, g/ncbm of active constituents	125	85	95	90
% gasol in the yield	13	13	12	16
Boiling range:				
% by weight of gasoline	20	20	20	40
" " " " oil	13	30	40	38
" " " " paraffin	67	50	40	22
Olefines:				
% by volume in gasoline	80	86	88	87
" " " " oil	74	82	81	82

Table 10:   Simultaneous Change of Catalyst
in Method of Operation

Catalysts	C	D	E
Pressure, atm gauge	10	15	20
Gas	water gas	water gas	CO-rich gas
% CO	39	39	50
% H_3	48	48	38
% gasoline by weight	81	39	14
" oil " "	13	31	22
" paraffin " "	6	30	64
Olefines:			
% by volume in gasoline	70	67	80
" " " " oil	65	58	73
Octane number (Primary gasoline -200°C)	69	72	81 leaded

Table 11: Displacing the Consumption
Proportion of CO:H₂

Catalyst	B9	B10	B4	B5	B6	B7	B8	C
Gas			──────→ Water gas ←──────					CO 50.9%
Pressure, atm gauge			──────→ 20			←──────		H_2 38.1%
method of operation			──────→ I			←──────		II
Consumption proportion: $CO:xH_2$	158	151	125	117	105	0.97	0.88	0.71 (to 0.6)
Boiling range:								
gasoline	52	45	16	22	33	45	25	20
oil	26	28	18	22	23	20	20	13
paraffin	22	27	66	56	44	35	55	67
Olefines:								
in gasoline	52	54	64	63	65	69	79	80
in oil	46	48	56	55	54	63	75	74

Table 12: Paraffin Synthesis with Water Gas

Catalyst: B4
Gas: water gas with 38% CO and
       48% H_2 (1:126)
Pressure: 15 atms
Temperature: 230°C
Contraction: 60%
CO conversion: 80%
CO as CO_2: 25.6
CO as CH_4: 7.0
CO gasification: 67.4
H_2 conversion: 80.0
CO + H_2 conversion: 80.0
Consumption Proportion:
   $CO:H_2$ 1:1.24

Yield g/ncbm active gas ingredients

	1st stage	2nd stage	1st and 2nd stage
	experimental	calculated	calculated
Gasol	10	3	13
Liquid products	135	20	155
	145	23	168

Table 12:   Paraffin Synthesis with Water Gas (Cont'd.)

	1st stage	2nd stage	1st and 2nd stage
	experimental	calculated	calculated
Boiling range:			
gasoline	-200°C	16% by wt.	about 70% olefines
oil	200-320°C	20% " "	" 70% olefines
soft paraffin	320-460°C	22% " ")	
hard paraffin	over 460°C	42% " ")	64%

Table 13:   Comparison of the Most Favorable Single Results
            with the Iron and Cobalt Catalysts

Catalysts	Fe	Co
Yield, g/cbm, 1st stage	145	130
Yield, g/cbm, 1st and 2nd stage	168	155
Boiling range:		
gasoline -200°C by weight	60	60
oil 200-320°C	40	30
paraffin, over 320°C	70	70
Olefines:		
in gasoline	90	65
in oil	82	55
Octane number (primary gasoline -200°C)	72	57-65