SINCLAIR REFINING COMPANY

Reel 26   (Re: Precipitated Iron Catalyst
Bag 2463-9   a) Reduction & Preparation of 1639
900000282-87   I.G. Standard Catalyst
                    b) Fischer-Tropsch Process
                    c) Copper Addition Stabilizes
                       Hexagonal Carbide Fe_2C)

S-4

Conference of Group-Leaders (3-31-1943)

Re: Paraffin-Synthesis

Research projects in regard to the conversion of carbon monoxide and hydrogen according to the Fischer-Tropsch process, were initiated because we were anxious to get a picture of this process based on our own tests. Furthermore, we were going to try to develop less expensive new catalysts of optimum activity by changing systematically the composition of our catalysts.

It is well known that up to this date the Fischer cobalt catalyst consisting of cobalt and kieselgur in a 1:1 ratio with 18% of thorium oxide, based on the metallic cobalt, is in commercial use for the pressureless and medium-pressure synthesis. Nowadays, a part of the thorium oxide (about half of it) is being replaced by magnesium oxide.

While we studied these contacts, it became more and more important to direct the reaction in such a way that as the main product, a paraffin suitable for the paraffin oxidation, would be formed.

When the war began we had succeeded in developing a cobalt catalyst which yielded about 70% of the primary product in the form of straight-chained paraffin with a boiling point of 320°, that is, with a chain length of more than C_{18} (in the laboratory at medium pressure, 12 atm). This cobalt paraffin is snow white; it contains only slight quantities of olefins and alcohols, about 3-5%.

When the war started, the use of cobalt turned out to be a very dubious proposition. Now we were once more confronted by the same task: to find a new catalyst, this time on an iron basis.

The actual literature, including the patents, is most exiguous, although the matter of cobalt replacements became ever more urgent in the course of the war. That tends to show that, after all, we met with greater difficulties in developing iron catalysts than we had anticipated. The new iron catalyst was supposed to be simple to prepare, easy to reproduce, to yield the same products at the same ratio as the cobalt catalyst.

This iron catalyst ought to be forthwith useable, that is, if possible without requiring farther reaching adaptations of the actual plant units; that means, it ought to operate within the temperature range of the reactors.

What difficulties are raised by these demands?

1.) First, iron contacts show a different reaction scheme. It is well known that the carbon monoxide hydrogenation can take place in two directions:

$$CO + H_2 \longrightarrow CH_2 + H_2O \qquad 2CO + H_2 \longrightarrow CH_2 + CO_2$$

Now, cobalt catalyst conversions follow exclusively the former equation. With iron catalysts, however, the conversion takes place according to the latter equation. At least, that is what the literature says. According to our experiences, however, the actual behavior in practice follows the added up equation of both #1 and #2:

$$3CO + 3H_2 \longrightarrow 2CH_2 + H_2O + CO_2$$

More recent observations and considerations let it even appear feasible that iron catalysts, too, start by reacting the feed-stock constituents according to equation #1; but later on, a partial conversion will go on at the iron catalysts at a comparatively low synthesis temperature: $CO + H_2O \longrightarrow CO_2 + H_2$, so that as the total reaction the conversion reaction #3 results from the two conversion equations.

What conclusions may be drawn from this unorthodox behavior of the iron catalysts?

They require a feed stock of quite a different composition than the cobalt catalysts do. Whereas these catalysts require a stock consisting of $CO:H_2 = 1:1$, the iron catalyst requires one having the ratio 2:1.

Furthermore, in the presence of the cobalt catalyst comparatively easily condensable products are formed, whereas in the presence of iron catalysts the exit gas will contain larger quantities of carbon dioxide. For instance, pursuant to equation #3 at an 80% conversion rate the exit gas contains 40% of CO_2. In order to maintain constant high CO and H_2 partial pressures at a multiple-steps operation scheme, under certain circumstances, a carbon dioxide wash may become necessary.

While the first type of difficulties is originating from the different reaction scheme, the second type is originating from the very disparity in the activities of the two catalyst metals.

Fresh cobalt catalysts operate, in general, starting with 160°, at a once-through passage with the technically usual charge of one l of stock per one g of cobalt metal; they achieve a conversion rate of approximately 90% at 190°. In the course of continuous operation this temperature must slowly be raised to 205°. These experiences were available when the converters were erected. The reaction is well known to be of a strongly exotherm character. A large quantity of reaction heat is developed and must be removed as quickly as possible, in order to prevent the catalyst from getting overheated. If we fail to do so, overheated areas develop on the catalyst which generate excessive methane formation, that is, they promote rather the hydrogenation of the methane radical than its polymerization to long-chained hydrocarbons. For the purpose of carrying off the reaction heat, the converter has been developed as a tubular furnace, in which the catalyst is cooled by means of boiling water. Technically a maximum water vapor pressure of 25 atms is allowable, that is, a catalyst temperature of 225°. Now, these facts mean that it was easy to reach the maximum temperature of about 200° required for cobalt catalysts. But the iron catalysts developed by the various plants up to this time, do not permit such temperatures, even when operated with a substantially lesser charge per gram of metal (0.4 l/g Fe). Under favorable conditions we may just succeed in attaining 220°; thus, there is no temperature reserve for more prolonged operation periods.

That is more or less the present situation in regard to the task of replacing cobalt by iron in our actual/fuel plants.   motor

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In regard to our own research studies the situation was insofar different as we have always believed that new hydrogenation units will have to be erected for the production of paraffin. For this purpose reactors would be required, which would stand a higher water vapor pressure. For this reason, a higher reaction temperature did not scare us. Of course, we were also anxious to attain the lowest reaction temperatures possible, as long as they would not prejudice the paraffin production. At present, of course, we shall follow up all experiences which are pointing towards the possibility of lower synthesis temperatures. It is a lucky coincidence that Dr. Kaertkemeyer is running some very promising tests by means of varying the composition of our standard catalyst.

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We shall discuss our experiments in somewhat greater details and point out problems and observations which might be of more general interest.

Pressure: - - - Ever since our cobalt studies, we operated at a superatmospheric pressure of 12 ats. The transpiration manometer developed by Dr. Kotzschmar proved to be very useful for small scale tests. It enables us to measure even the smallest quantities of a single gas under pressure. For the measurement of larger gas quantities we have dry-gas meters built-in into pressure containers according to the Leuna model. They are not yet quite satisfactory. For our commercial experiments a well developed equipment is available.

Gas Mixture: In the laboratory we are using a synthetic mixture containing about 2% of inerts and no CO_2. In the pilot plant we are using the exit gases of the tanol-plant.

Converter: For our small-scale tests, we are using pressure tubes of a length of 5 m, and of an interior diameter of 15 mm, which are placed into an oil bath working as a heating agent and which can be connected in steps one behind the other. In the pilot plant is a 1 m^3 converter, supplied by Ruhrchemie. Because of its welded-in displacement tubes, it caused much trouble. Recently it has been displaced by about 700 single tubes of a length of about 4 m and of an interior diameter of 15 mm. They have no displacement tubes.

Reduction: The built-in iron catalysts are reduced with hydrogen approximately at the synthesis temperature, that is, at 225° for 24 hours with a volume charge of 1000:1. The linear velocity in the 5 m^3 reactors is about 120 cm/sec. They can be reduced with synthesis stock, too, particularly on selecting a very high volume charge. Therefore, a separate reduction operation may be omitted, and the converter may be started directly for the synthesis operation. Recently, however, no tests of such a type were made.

Catalysts: Three types of catalyst were studied:

    a.) Fused catalysts: reaction favors olefins & alcohols.
    b.) Sintered or roasted catalysts: low-boiling alcohols.
    c.) Precipitated catalysts: paraffin.

    Since I am going to limit my report to the problems connected with the paraffin production, I shall discuss only precipitated catalysts.

    Among the great number of catalysts examined by us, two have gained special distinction:

    1.) An alkalinized iron-copper-aluminum oxide catalyst.
    2.) An alkali iron-copper-magnesium oxide kieselgur catalyst.

    Each one of these catalysts shows advantages and disadvantages.

The aluminum catalyst shows the following disadvantages: precipitation is cumbersome, taking three days; hard to wash out; no decanting possible.

Its advantages:

The paraffin is practically identical with that formed in presence of the cobalt catalyst in regard to its quality. Yields about 50% of the primary product. Straight-chained 92-95%. Low synthesis temperature, about 15° below the temperature required in the presence of the magnesium oxide catalyst.

The magnesium oxide catalyst shows the following advantages:

It can be quickly and simply prepared. It is easy to reproduce. High paraffin yields of 65-75%.

Its disadvantages:

The paraffin is not quite as straight-chained as that produced in the presence of the cobalt catalyst, depending upon the charging. On the basis of a 120 l charge, for instance 80-82% straight-chained paraffin is obtained in the four-steps process. The product contains many olefins, some alcohols.

Because of its yielding a larger paraffin portion we adopted the magnesium oxide catalyst for our further studies. For this reason we are calling it our "standard catalyst."

It is prepared in the normal way by precipitating the nitrate mixture with potassium carbonate by adjusting the alkali contents in the mother liquor by means of decanting; it is pressed, predried on a groove drum constructed by Dr. Wisenia, and finally dried at about 80°C. in the vacuum drying chamber.

One additional remark must be made concerning the constituents:

Copper:- Already about 12 years ago Fischer added some copper to his iron catalyst for the purpose of promoting its reduction. X-ray studies were begun by Dr. Halle and were continued by Dr. Herbst. They showed that copper does not only promote the reduction but that it has also a very important role in the synthesis. In the synthesis a hexagonal carbide Fe_2C is generated which has not been yet described in literature.

We consider it to be necessary for the good activity of the catalyst. In the course of time, particularly at higher temperatures, this novel hexagonal carbide, which Dr. Herbst had found, turns into the well known Haegg carbide Fe_2C. This transformation is considerably checked by the copper addition, so that we can regard it as a stabilizer of an intermediate phase of the catalyst, which develops only during the synthesis. For instance, on adding 2% of copper the Fe_2C transformation temperature lies 50° higher.

Kieselgur: Kieselgur has proved to be a rather desirable carrier. But because of the heterogeneity occurring even with the very same brands, it has caused us much trouble. We are using a wind-sifted brand 4S, which we ignite for 2-3 hours at 600°; we are very satisfied with this method. Narrowly porous Kieselgel A has proved to be highly desirable; in order to prevent reactions with the metal oxides, it must be ignited, too, at 800-1000°.

Catalyst Charges

Because of the varying densities of the iron catalysts, it is expedient to base the charge on the volume. For catalyst tests we used a charge of 720:1/hr, with a heaping weight of 0.45 and an average iron content of the catalysts of about 25%, that is about 6.5 ltr/1 g of iron metal. We think that with such a high charge we are in a better position for observing any differences that may occur.

Synthesis

The rate of the conversion of carbon monoxide into the desirable hydrocarbons depends to a large extent upon the temperature prevailing. We observed that initially the catalysts would promote rather the formation of water. The longer they are in service, the more the formation of carbon dioxide will prevail. The separation of the products takes place usually in steps: at 120° (paraffin) - 20° (oil) - 0° - 70° (gasoline, dissolved gasol).

Yields:

It would be superfluous to mention the figures for small scale tests. But I shall give the figures for a four-steps-preliminary test, which is still going on at the present time:

At a total charge of 120:1, without removing CO_2 at 230° we obtain yields of 150 g/ N m^3 with a CO consumption of 84%. The proportion of $CO_2:H_2O = 1:1$.

The boiling range fractions are distributed as follows:

	olefins	alcohols	straight-chained	
-195°C.	25%	52	11	55
250-320°	12	44	10	70
-450°	22	35	8	83
450°	41			

The space volume yields are 0.45 kg/l contact chamber/day. In the course of several weeks the yields decrease somewhat, but the hard-paraffin portion decreases still faster.

These figures show that we succeeded, to a certain extent, in developing an iron catalyst which forms about the same quantity of paraffin as the cobalt catalyst. But the quality of its product is not quite as desirable because it is not quite so straight chained. The olefin contents would not bother us; on the contrary, we are anxious to prepare a product having much higher olefin contents. We could use its middle-oil fraction for the Oxo-reaction and the paraffin fraction, after its being hydrogenated for the paraffin oxidation.

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