SINCLAIR REFINING COMPANY

Reel 26

Bag 2463 Item "N"
Frame 900000297-301

(Re: Preparation of Precipitated
Iron Catalysts)

1040

S-5

To the Manager of the Four-Years-Plan
General Plenipotentiary for special chemical-production problems
Care of Dr. Altpeter

re: Cobalt supply / your letter January 16, 1943.

     We are referring to your aforementioned letter, addressed to our High-Pressure-Development Department. We learned through Dr. Kranepuhl that you do not ask for an iron catalyst exhibiting exactly identical properties as the Ruhrchemic cobalt catalyst, but that you want information concerning the general possibilities, inhowfar an iron catalyst can replace the cobalt catalyst, and how the available equipment, etc. may be adjusted to the different synthesis conditions resulting from this substitution.

     We think that, up to this date, an iron catalyst could not be substituted for the cobalt catalyst because the converters in actual service are limited to a reaction temperature of about 220° because of the water partial pressure. We assume that this is still the essential issue, and that, therefore, we ought to try to find an iron catalyst not exceeding this temperature range, even at the end of its operation period. In this report we are describing a catalyst which may be most suitable for replacing the cobalt catalyst. However, there are still some objections to be raised which we shall not omit to mention. It is a catalyst developed in the Ammonia-Laboratory at Oppau. Jointly with the Ammonia Laboratory we have examined the possibilities for employing this catalyst, and we shall describe the essential points resulting from the prior experiments at Oppau.

Catalyst

     It is a precipitated iron catalyst, containing small quantities of copper, potassium, MgO and Kieselgur / we shall call it the "standard catalyst". The "heaping weight" of the catalyst is 0.42; 60 kg of copper are needed for one ton of catalyst. A size of 2-4 mm for the granules is suitable. Its solidity is much greater than that of the Ruhrchemic cobalt-catalyst. It has been tested in small laboratory converters. Furthermore, a four-steps test was run with 4 iron tubes of a length of 5 m each, having an interior diameter of about 15 mm. The reaction heat was carried off by means of circulating oil. Into each tube 0.8-1.0 l of reduced catalyst were filled in. Actually, we are running another test in a converter having approximately a capacity of 600 l of catalyst / the individual tubes have an interior diameter of 15 mm without displacement tubes; boiling water is used as a cooling agent.

Reduction

     The catalyst may be reduced with hydrogen as well as with the water gas used as feed stock in the very convertor ($200-230^\circ$). After a period of approximately five days it reaches full activity. Thus, it is no more necessary to reduce the catalysts from a central place with a special stock. However, one may consider the advisability of reducing the catalyst in a special reactor before introducing it into the converter, in order to utilize more fully the capacity of the convertor because in this way full activity starts faster.

Synthesis Conditions

The catalyst works best under a pressure of 12 ats. or more. However, one may also operate at 10 ats. It is expedient to use a feed stock containing 50:50 quantities of CO and H_2.

The organic and anorganic sulfur must be carefully removed, just as with a cobalt catalyst. However, we have the impression that the iron catalyst is not quite as sensitive against organically bound sulfur as the cobalt catalyst is.

Synthesis Temperature

In our small laboratory convertor we operated at a temperature of 250° with a catalyst charge of 240:1 and a CO consumption of about 30%.

With the four-steps-operation scheme and with a total charge of 120:1, at this temperature of 250°, a total CO-conversion rate of 84% has been achieved (output about 150 g/Nm^3; space/time/yields 0.45/1/day). Taking into consideration that this space/time/output is higher than that of the actual cobalt catalysts, one may expect that on proportionately reducing the total catalyst charge, the conversion temperature could be reduced, too. We are at this date unable to state, whether the temperature could be reduced to much less than 220°, while still keeping a sufficient temperature reserve. The 10 m^3 Oppau converter is built for a 40 ats. vapor pressure, corresponding to a temperature of 250°. That is why Oppau is assuming that we may figure with this temperature limit.

Recently we succeeded in the laboratory in obtaining lower conversion temperatures by using various additives. This reduction in temperature, however, was achieved at the expense of a reduction in paraffin yields. That is why we failed to follow up this line. However, it might be done in special cases.

	Temp.	CO-conversion rate	Hr./cat./charge	Paraffin	320°
New Catalysts	220	35	720:1	12	
Standard Catalysts	220	19	720:1		75

The same is true for the standard catalyst in regard to the correlation between a reduction in temperature and an increase in the yields of lower-boiling products, which may be achieved on increasing the kieselgur portion and on decreasing the MgO contents, or, perhaps, we might even totally omit MgO.

It is a feature of the standard catalyst that it produces a comparatively large portion of higher boiling products. Sometimes up to 70% of products are attained which boil at more than 320°. Therefore, we may call this conversion in the first line a "paraffin conversion". The total product is composed as follows:

(Four-steps-process. 677-680 - at 230°C.)

-195° :	Benzene	26%
-320° :	Middle Oil	12%
-450° :	Paraffin	19%
over 450° :	Paraffin	43%
		100%

Another difference must be mentioned in this connection. With cobalt catalysts, practically no oxygen-containing compounds are obtained and few un-saturated compounds. But with this catalyst we obtain an alcohol content of about 10% and 50-55% of olefins among the total products. Our tests showed that this alcohol content does not disturb the paraffin oxidation. We may also assume that it has no influence on the Diesel oil range. To be sure, the property of the oil making it an improving addition for low-quality oils, will thereby suffer. Within the gasoline fraction the oxygen contents will not mean any deterioration, either.

Yields

By using water gas, the output has been somewhat increased. At the Oppau tests our synthetic gas mixture (48.5% CO, 48.5% H_2, 1.0% CH_4, 2% N_2) has been reacted in four steps, and thereby practically 140-160 g/m^3 of products were ob-tained, without intermediate carbon dioxide removal. The solid and liquid pro-ducts, however, such as gasoline, middle oil, paraffin, were removed after each step.

Intermediate feed-stock Treatment

We are repeating our statement made in our letter of February 10, 1943; whereas, in the presence of a cobalt catalyst, the oxygen-contents of the stock will practically be eliminated only as H_2O; in presence of an iron catalyst, half of them will appear as CO_2 in the final product, and half of them as H_2O. For this reason, a stock having CO:H_2 1:1 is used as a starting material; if it is converted in this ratio, as is the case with the standard catalyst, the exit gas is forthwith ready for the next step.

We found that the standard catalyst is comparatively insensitive against CO_2. Therefore, we may hope that, perhaps, the CO_2 wash in between the steps can be avoided. But we must remember that, up till now, Oppau has operated with CO_2-fee stock. Tests will have to show how technical water gas will react.

(The rest of the text is referring to the actual lack of personnel, etc. - MB)

(In Reels 302-7 the same information is repeated with a slightly different wording. They have not been translated. - MB) (Frame 308 contains the following addition - to April 17, 1943)

For the purpose of finding an iron-catalyst substitute for the cobalt catalyst used in our actual converter units, we were recently studying the effects of adding halogen compounds, particularly in the form of fluorine compounds. Prior tests had shown them to work at lower temperatures than the precipitated catalyst, MgO - kgr (standard catalyst) which we had used for the paraffin synthesis.

On reducing the alkaline contents of the standard catalyst - to be sure, without reducing the temperature - the primary products will contain substantially less higher-boiling portions, but considerable quantities of alcohols.

In all tests, we operated with the same charge of about 720:1, that is, about 6.8 l/hr./1 g of iron, as against the usual charge of 4 l/hr. 10 g of iron.

	Standard Catalyst		Standard Cat. less Alk.		Standard Catalyst Having Ca F$_2$ instead of Kieselgur
Experiments No.	693, 694		674		631
Catalyst No.	1298	2	1459		1389
Temperature	220	230	220	230	220
g Yields/Nm^3	12	42	18	40	50
CO-conversion rate	12	20	12	24	35
Boiling Range - 195°		10	26	36	47
- 250°		6	27	16	22
- 320°		10	17	15	15
- 450°		18	19	18	9
over 450°		56	8	13	3
Total		100	97	98	96
Middle Oil Fraction 250-320°					
% Olefins		46	29	30	25
% Alcohols		25	52	81	39
Paraffin Fraction 320-450°					
% Olefins		36	30	27	19
% Alcohols		18	53	35	16

In view of the fact that the standard catalyst produces yields of 150 g/Nm^3 in a four-steps-operation scheme at 230° and at a 120:1 charge, we shall be justified in assuming that the fluorine-containing catalyst will produce the same yields already at a lower temperature (220°) under the same conditions.

Further Projects

As the four-step-test seems to prove that carbon dioxide does not injure the life of the catalyst we shall try to obtain a maximum output in a once-through test in a converter with the same charge. We shall run the same test with the fluorine-containing catalyst.

Further catalyst combinations will be tested in the 1 m^3 converter, when we shall have overcome certain difficulties in separating the primary products.

In case Dr. Koelbel should visit the Ammonia Laboratory at Oppau, he can be shown only the small experimental converter with oil-recycle-heating, the 5 m - converters of the four-steps-test, one 5 1 - converter with boiling-water cooling and a 1 m^3 - converter from Ruhrchemie.

G. Wietzel

M. Beth

MB/es