

UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
OFFICE OF SYNTHETIC LIQUID FUEL
LOUISIANA, MISSOURI

1286

TOM Reel No. 49, Frames 533 - 540

T-423

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December 1, 1947

BRIEF REPORT OF THE KAISER - WILHELM - INSTITUT FOR
INVESTIGATION OF COAL MULHEIM - RUHR
IN THE FIELD OF MIDDLE PRESSURE SYNTHESIS WITH IRON
CATALYSTS

The Middle Pressure Synthesis with Iron Catalysts:

The K.W.I. in Mulheim has found in 1937 that the cobalt catalysts used for the hydrocarbon synthesis could be replaced with iron catalysts if the synthesis was to be done under pressure of the range of the middle pressure synthesis with cobalt catalysts. The stability of the iron catalysts was found to be very good. For a good yield of the higher hydrocarbons at the lowest possible temperatures the proper pre-treatment of the catalysts was very important. It was designated as "forming" and was carried out at a lower pressure than the operating pressure during synthesis, e.g. at atmospheric pressure when working with synthesis gas.

The new method of forming the catalysts resulted in an advantage against the older tests, in which the yields with the iron catalysts were entirely unsatisfactory.

Originally precipitated iron - copper catalysts were used in tests with middle pressure synthesis with iron catalysts, as has already been done previously in normal pressure synthesis. It has been found soon, however, that with a proper pre-treatment of the catalysts, copper as well as other additions could be largely dispensed with, and occasionally even entirely eliminated, without causing through it any deterioration of the yield in higher hydrocarbons.

At present work is mostly done with catalysts precipitated from a solution of iron nitrate with soda and containing 1 percent copper as well as 0.25 percent

potassium carbonate, referred to iron.

Communications, Patent Applications etc.:

The experience of the K.W.I. in the field of the middle pressure synthesis with the iron catalysts was communicated to the licensees of the gasoline synthesis at two meetings in the large lecture room of the Institut in Dec. 1937 and Sept. 1940.

The basic facts of the middle pressure synthesis with iron catalysts have been described in the following patent applications:

1). St. 56,470, IV d/12 0 (July 30, 1937)

As an example quoted in the patent application, a precipitated iron-copper catalyst with 20 percent Cu is first pretreated with 1/8 percent potassium carbonate and with hydrogen-rich synthesis gas at atmospheric pressure, and next used in operation at a pressure of 15 atm.

2). St. 56,856 IV d/12 0 (Nov. 23, 1937)

This application refers to iron catalysts which can in a very general way be prepared by a decomposition of iron compounds. Claim 2 of the original application specifies a pressure of 5 - 50 atm. as the optimum synthesis pressure. Claim 3 refers to a pretreatment of the catalyst at normal pressure, or a lower pressure than the subsequent operating pressure. In contradiction to the first application, it has been expressly stated here, that the pretreatment of the catalyst must be done in a gas containing CO.

3). St. 58,896 IV d/12 0 (June 30, 1939)

This application specifies iron catalysts to synthesis after a pretreatment with synthesis gases containing carbon monoxide at reduced pressure. Such a preparation produces particularly active catalysts.

4). St. 60,409 IV d/12 0 (Jan. 21, 1941)

The composition of the synthesis gases was left open in the former applications, merely stating that they were water gas or carbon monoxide-rich synthesis gas; a high-hydrogen synthesis gas is specified in this,

application. They permit operations at particularly low pressures.

5). St. 60,795 IV 2/12 0 (May 23, 1941)

Some important details of the preparation of iron catalysts are described in this application, and in particular, that the catalysts must be prepared from specified solutions of iron nitrate, first neutralized in the cold or at temperatures below 50°C, and only then heated for the precipitation.

6). German Patent 708,500 (March 14, 1937)

The patent protects a method of leading in the gas during the catalytic reductions. The gases are first made to hit a gas-permeable wall, e.g. of perforated sheets, with the catalyst placed on the other side of the sheet. This method of operation results in no loss of the reaction velocity and eliminates inconveniences connected with resistance offered to the synthesis gases by the catalysts.

When catalysts tubes of circular cross section are used, perforated sheets are usually introduced, which separate a small section of the cross section from the catalysts space as a gas space. When ring shaped catalyst space is used, perforated tubes can be introduced in a corresponding manner, which again separate a small part of the available reaction space from the catalyst space, as gas space.

A number of other facts about middle pressure synthesis, which have not been used for patent applications have been discussed at the meetings mentioned above, as e.g. the improvement in the activity of insufficiently active catalysts by treating them with hydrogen.

The minutes of the meeting of Sept. 10, 1940, have already been sent to the Ruhrchemie. A voluminous summary of experiences gained since June 1940 by the K.W.I. in the field of middle pressure synthesis with iron catalysts is translated as T - 424.

From 1937 to 1940 the yields at synthesis temperatures of 230 - 260°C amounted as a rule to 140 - 160 g/nbcm of synthesis gas, with the proportion of hydrogen to CO maintained the same as their consumption, and 140 g yields were still realized after 1-1/2 years of operation

in a single stage, without reactivation of the catalyst.

The question was asked in the beginning of 1943 about the extent to which the reactors for the middle pressure synthesis with cobalt catalyst could be applied to synthesis with iron catalysts, with a permissible maximum pressure of 10 atm and a permissible maximum temperature of 225°C, and the K.W.I. replied with a short report of conditions which are particularly favorable in operations at lowest temperatures, and at the same opportunity reported the results of some laboratory experiments performed with high-hydrogen synthesis gas.

Semi-Technical Experiment with High Hydrogen Synthesis Gas

As a complement to the report sent in April this year to the Ruhrchemie on the middle pressure synthesis with iron catalyst using extremely high-hydrogen synthesis gas, we may say that the first step of an experiment with an extremely high hydrogen concentration in the synthesis gas ($\text{CO} : \text{H}_2 = 1 : 4$) has been run in the meantime on a semi-technical scale for two months (19 tubes with perforated sheet inserts, 4.0 l reaction space, water cooling, precipitated iron catalyst with 1 percent copper and 1/4 percent cobaltum carbonate, with the catalysts prepared as in St. 60,795). The reactions were conducted at 185 - 190°C. The conversion remained absolutely constant during the whole test, with the temperature maintained at the same level. The first stage produced 55 g liquid products in gasol/nobm. The purpose of the tests was to obtain a somewhat larger amount of products than are normally produced on iron catalysts at extremely low temperatures. The products differ from those obtained on a laboratory scale in aluminum block reactors by the production of a larger amount of higher boiling hydrocarbons and a smaller amount of gaseous products. 24 percent of the liquid and solid reaction products obtained at 185° consisted of solid paraffine, 10 percent of alcohols and 20 percent of $\text{C}_3 - \text{C}_4$ hydrocarbons. 50 percent of the $\text{C}_3 - \text{C}_4$ hydrocarbons were unsaturated.

Example of a Method of Operations Permitting the Use of Iron Catalysts for Synthesis in the Earlier Cobalt Middle Pressure Reactors

Different variations are possible in the middle

pressure synthesis with iron catalysts by varying the composition of the catalysts, of the synthesis gas, the supply of gas, and other conditions. They are not in principle important for synthesis, but permit the adjusting of synthesis to requirements made by the industrial realization of the process. There are several ways of meeting the latest requirements of synthesis with iron catalysts, using the earlier cobalt middle pressure reactors. When selecting these ways it pays to start with certain limitations by operating with the simplest catalysts in composition, if no important disadvantages will result; i.e. with catalysts which contain no large amounts of the more costly constituents of metals the supply of which is at present limited, in addition to iron.

We may say with respect to the composition of the synthesis gas that as the amount of hydrogen increases the reaction temperatures may be lowered, but that there exists here in practice a limit, when it becomes uneconomical to pass an all too large dead balance of hydrogen through the synthesis equipment. If one were for instance forced to operate a temperature of 190°C , a 1 : 4 proportion of $\text{CO} : \text{H}_2$ would have to be used, while at $200 - 210^{\circ}\text{C}$ the best synthesis gas in the long run will have a proportion of $\text{CO} : \text{H}_2 = 1 : 2$, and finally at a temperature of 220°C the normal water gas may be used as synthesis gas.

These data refer to a thruput of 10 li of synthesis gas/10 g of iron/h. When the gas thruput is reduced the operating temperatures may be lowered. Thus with a thruput of 2 li of water gas/10 g of iron/h a satisfactory conversion is already obtained at 210°C .

It does not appear desirable to start operations of the synthesis apparatus near the upper temperature limit, and it is important to select operating conditions during which yields will not alter with a given gas thruput over a long time interval of at least a number of months.

We give below an example of an operating procedure with a synthesis gas having a $\text{CO} : \text{H}_2$ ratio of 1 : 2 and at which the operations can be conducted at synthesis temperatures of $200 - 210^{\circ}\text{C}$.

1. Synthesis Equipment

The present cobalt synthesis reactors are used.

It is however advantageous to insert perforated sheets, or tubes in case of ring shaped reactions, which separate about 1/4 of the space as gas space.

2. Catalysts and its Preparation

Precipitated catalysts are used, such as an iron catalyst with 1 percent copper and 1/4 percent potassium carbonate (prepared according to the patent application St. 60,795).

The catalyst is pretreated with gas consisting of carbon monoxide or a mixture of carbon monoxide and hydrogen at some lower pressure than the synthesis pressure. The forming at the reduced pressure produces the most active iron catalyst which will therefore require the lowest operating temperatures. If an iron catalyst has been "incompletely formed" at normal pressures, its activity may be increased by subsequent, and if necessary repeated hydrogen treatment (see directions in the report of Sept. 10, 1940, T-424). Such treatment with hydrogen may be done at the synthesis temperature.

3. Synthesis Gas Composition

CO : H₂ = 1 : 2

4. Synthesis Gas Pressure

10 atm.

5. Operating Temperature

205 - 208° (400 li synthesis gas/h/kg iron)

6. Course of Synthesis

In stages maintaining the CO : H₂ ratio after the individual stages by adding water gas, following a scheme shown in the table below.

0.725 ncbm water gas and 0.275 ncbm hydrogen (1 ncbm mixed gas with CO : H₂ = 1 : 2) are used in the first stage. 0.54 ncbm end gas from the first stage and 0.55 ncbm water gas are passed through the second stage. The third stage contains 0.64 ncbm end gas from the second stage and 0.49 ncbm water gas. The contraction, carbon monoxide and hydrogen utilization

as well as the yields from the first, second and third stages can be seen in the table.

Summary

After presenting briefly the work of the K.W.I. on the middle pressure synthesis with iron catalysts, conditions are discussed which permit carrying out the synthesis at the lowest possible temperatures. This is illustrated on an example, according to which a synthesis gas with the ratio of $\text{CO} : \text{H}_2 = 1 : 2$ is converted at temperatures between $200 - 210^\circ$ in several stages.

The use of higher-hydrogen synthesis gas is particularly advantageous for the stability of the iron catalyst. Using the cobalt middle pressure reactors for synthesis, the requirements may be met by using water gas as synthesis gas. With a normal thruput (4.11 water gas/10gfe/h the reaction temperature is around 220°C , and it can be lowered to 210°C with a reduced gas thruput.

Mulheim Ruhr, July 13, 1943

Kaiser Wilhelm Institut für Kohlenforschung

/s/ Prof. Fischer

-8-

T-423

The Course of Middle Pressure Synthesis with Iron Catalysts,
a Synthesis Gas with a CO : H₂ ratio of 1 : 2, in Several
Stages, Re-forming the CO : H₂ ratio of 1 : 2, after each
Stage by the Addition of Water Gas.

(Precipitated iron catalysts with 1 percent copper and 1/4 percent potassium carbonate; synthesis pressure: 10 atm; synthesis temperature 205 - 210°C; velocity of flow: 4 ii synthesis gas/10gFe/h).

0.725 ncbm water gas

0.275 ncbm hydrogen

1.0 ncbm (CO : H₂ = 1 : 2)

1st. Stage

Contraction:	46 percent by volume
CO utilization:	81 " " "
H ₂	48 " " "
Yield (solid, liquid products and gasol):	94 g

0.54 ncbm end gas from first stage

0.55 ncbm water gas

1.09 ncbm (CO : H₂ = 1 : 2)

2nd. Stage

Contraction:	(1st. + 2nd. stages) 59 percent by volume
CO utilization:	(1st. 2nd. stages) 89 " " "
H ₂ utilization	(1st. + 2nd. stages) 65 " " "
Yield	(1st. + 2nd. stages) 130 g

0.64 ncbm end gas from second stage

0.49 ncbm water gas

1.13 ncbm (CO : H₂ = 1 : 2)

3rd. Stage

Contraction	(1 + 2 + 3 stages) 64 percent
CO utilization	(1 + 2 + 3 stages) 93 "
H ₂	(1 + 2 + 3 stages) 76 "
Yield	(solids liquids gasol) (1 + 2 + 3 stages) 144 g

0.73 ncbm end gas from the 3rd. stage