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(54) CATALYTIC PROCESS FOR SYNTHESIS OF ORGANIC LIQUIDS

(54) PROCEDE CATALYTIQUE POUR SYNTHESE DE LIQUIDES ORGANIQUES

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The present invention relates to an improvement in the methods of carrying out the catalytic union of carbon oxides and hydrogen to produce hydrocarbons of more than two carbon atoms and oxygenated derivatives thereof and more especially the invention relates to the method of conducting the reaction with catalysts in fluidized form and to such catalysts themselves. The invention will will be more fully understood from the following description and drawing.

The drawing is a semi-diagrammatic view in sectional elevation showing an apparatus for the reduction of carbon monoxide with hydrogen in which the catalyst is employed in a fluidized form.

During the past few years much attention has been directed to an improved method for conducting chemical reactions in the gas phase with catalysts in fluidized form, by which it is meant that a finely divided catalyst is dispersed throughout the reacting gas mixture to form a dense suspension which flows through the apparatus like a liquid, showing both dynamic and static heads. Such a system has been successfully applied on a large scale to the cracking of hydrocarbon oils and to other reactions as well.

It is of great importance to maintain the catalyst in the reactor in a good condition of fluidization since this insures uniformity of temperature and pressure throughout as well as constant conditions which lead to improved yield and efficiency in the operation.

In attempting to apply the system to the synthesis of hydrocarbons and oxygenated derivatives by the reduction of carbon oxides with hydrogen, it has been found that certain unexpected difficulties have arisen which appear to be peculiar to this particular reaction, especially when attempted on a large scale by which it is meant of a commercial size and considerably larger than would ordinarily be performed in the laboratory.

To illustrate the types of difficulties which are found, it may be stated that the size distribution of the catalyst particles has been found to be of great significance where it appears to be much less important in other reactions. In certain carefully controlled experiments, a suitable synthesis catalyst was duly fluidized in a synthesis gas at room temperature, that is to say below the temperature suitable for reaction. When the fluidization was satisfactorily accomplished, the temperature of the gas fed was gradually raised to reach the reaction range and to induce the synthesis of hydrocarbons and oxygenated derivatives. When, however, the reaction temperature was reached, fluidization became extremely poor with slugging and bumping. In other experiments it was found that hydrogen alone or CO alone could be employed to fluidize the catalyst even at the normal reacting temperatures, but on addition of the other reactant, CO or hydrogen as the case might be, fluidization suddenly stopped or became extremely poor in the zone of the reaction. It was finally found that in these particular reactions the process was much more sensitive than any others that had been previously studied and that it was a peculiarity of the reaction, not of the material being fluidized. The actual reasons and physical explanation of this are still obscure. It was found that the catalyst size distribution was of great importance and in this distinguished very sharply from the results obtained in the cracking of hydrocarbons and in other reactions. It was finally found that good fluidization could be insured in a stable condition throughout the operating temperature range by the selection of a proper balance of the size and amounts of the catalyst particles present in the reactor, and the present invention has for its object the definition of the proper range of size distribution for successful operation of the synthesis reactions with finely divided fluidized particles.

Referring to the drawing numeral 1 denotes a reaction vessel which is generally in the form of an upright cylinder with a conical base 2. A grid or screen 3 is located in the lower part of the cylinder so as to effect good gas distribution and in the upper portion of the cylinder a dust separator 4 is generally indicated. The separator is preferably of the type operating on centrifugal principles and the dust so separated is returned to the fluidized mass by the pipe 5 while the gas and vapor mixture is taken out by the pipe 6 to a scrubber condenser 7, fed with water by a pipe 8. The gas from which liquid products and final traces of catalyst have been removed is withdrawn by a pipe 9 and the liquid is separated in the vessel 10, water being withdrawn at the bottom by 11 and the hydrocarbon product by the pipe 12.

Within the reactor 1 it will be understood that the catalyst particles are distributed throughout the reacting gases in the form of a dense suspension, which comprises a denser phase below and a lighter phase above which are separated by a so-called interface or level which is indicated generally at 13. Within the denser phase cooling pipes 14 are located but it will be understood that they may be arranged in any preferred manner, not necessarily as shown.

Within this reactor the suspension is in vigorous motion which insures efficient utilization of the catalyst and accurate temperature control from top to bottom.

The gaseous feed consisting of the mixture preferably of two parts of hydrogen to one of CO is supplied by the pipe 15 through a heater 16 which is employed until the apparatus has been raised to reaction temperature. Thereafter the gas is preferably directed, or at least a part of it is directed, around the heater by means of a pipe 16. It will be understood that the reaction itself normally produces sufficient heat to maintain itself and, in fact, cooling by the pipes 14 is required.

At intervals a portion of the catalyst may be withdrawn by a pipe 17 as indicated and the catalyst may be separated from the carrying gas and regenerated or reworked as desired. Fresh catalyst may be supplied by the pipe 18, preferably in a carrier gas which may be a portion of the feed gas.

Considerable variation may be made in the apparatus for carrying out the reaction but in general that shown in the drawing is suitable. In any case, it should consist of an enlarged vertical reaction vessel provided with cooling means, fed with the reactant gases at the bottom. The catalyst is preferably separated from the gas within the reaction shell so as to maintain the bulk of the catalyst always within the reactor and to withdraw product vapors. After the separation of the liquid product from the gas, the latter may be recirculated to the reaction chamber, usually after a suitable adjustment of its composition.

In order to understand more fully the operation of the present process, it should be noted that the gas velocity upwardly in the reactor space is adjusted so as to maintain the distribution of the catalyst particles throughout the gas in a dense suspension. The velocity is preferably of the range of 0.2 to 1.0 feet per second, measured on the overall cross section of the vessel, although it may be as high as 10 ft. per second and will usually be between .5 and 5 ft. per second. When the pressure is elevated, say above 10 atmospheres, somewhat lower velocities are employed. This upward velocity is sufficient to maintain the catalyst in suspension. There is a considerable slip also between the catalyst and the gas, that is to say the catalyst particles rise considerably slower than the gas in which they are suspended. The temperature of reaction depends on other factors, principally the catalyst, but it is in the range of from about 350° to 675°F. With catalysts, the active element of which is iron, the preferred temperature is from 550° to 650°F., while with cobalt a lower temperature range from about 375° to 475°F. is preferred. With the iron catalyst it is preferable to use a pressure of 10 to 30 atmospheres where hydrocarbon production is to be emphasized and even higher pressures can be used if it is desired to increase the yield of oxygenated derivatives at the expense of the hydrocarbons. With cobalt-containing catalysts, atmospheric pressure can be conveniently used, although it is preferable to run from 5 to 15 atmospheres.

In regard to the catalyst size distribution, it has now been found that satisfactory operations, in which the fluidization is good and can be maintained stable, exist only under a relatively narrow range. This is not to say that no operation whatever can be maintained outside of these conditions but such operation is not smooth and it is subject to erratic periods in which the catalyst appears to rush upward through the apparatus in slugs and large bubbles or channels of gas pass through the dense catalyst mixture without adequate contact with it. The specification of the catalyst is as follows, it being understood that a uniform moderate spread of catalyst sizes is better than an extremely narrow range on the one hand and are extremely wide spread on the other. The entire catalyst is finely divided, in spite of the one portion designated as being over 80 microns, containing particles as small as 5 microns and less. The larger particles above 80 microns will be predominantly smaller than 100 mesh and will contain no particles larger than about 10 mesh.

Catalyst Diameter	Percent	Preferred
0 to 20 microns	Less than 25%	5 to 25%
20 to 80 "	30 to 85%	30 to 85%
Above 80 microns but still characterized as finely divided	Less than 45%	5 to 35%

The catalyst may be produced in many ways, first, for example, by grinding larger lumps of the catalytic material to approximately the proper size and then adjusting within the limits above mentioned by the addition of fines or coarse particles as required. Rough separations of ground catalyst may be made by air flotation or by other mechanical means and these rough fractions may be blended to give the desired distribution.

Catalysts in substantially spherical form can be made by forming a sol of the catalytic or carrier material, dispersing it in droplets in an inert gas or immiscible liquid, for example by emulsification, and maintaining it in this condition until the sol has set into a gel. It will be understood that the particles of sol are brought into spherical form under the influence of interfacial tension. If carriers are used such as silica gel, mixed gels, etc., they can be impregnated with the catalytic elements.

Catalysts of the above specification can be readily fluidized in a stable condition which is not subject to sudden erratic bumping and slugging, and the hydrocarbon synthesis process may be carried out smoothly and efficiently. Catalyst loss is not excessive; the yields of liquid product are greater than obtained during unsatisfactory fluidization, presumably because of the better distribution of the catalyst throughout the gas and more efficient temperature control.

Example I.

The apparatus employed in the present example was quite similar to that illustrated above. The reaction vessel was about 15" in diameter and 40' in height. Cooling was effected by 8 vertical cooling pipes connected at top and bottom by ring manifolds, each tube being 30' long and 2" in diameter, placed in the lower part of the reaction vessel and fed with the cooling fluid.

The various operations described hereinbelow were carried out in the reactor with from 200 to 1,000 pounds of catalyst comprising cobalt on an inert carrier and at atmospheric pressure or up to 20 lb. gage. The temperature ranged in different portions of the runs from about 380 to 410°F. The synthesis gas was made up of about two volumes of hydrogen to one of CO and contained some CO_2 and at times it was diluted with additional hydrogen. Temperature measurements were taken at several levels in the reactor and pressure manometers were also placed along the reactor at different levels. From the manometer readings, the height of the dense layer of catalyst could be readily determined as well as the total amount of catalyst in the reactor. The total run covered several weeks of operation and is divided into several periods wherein different sized catalysts were used under various conditions and different attempts were made to obtain good fluidization. It was found that when hydrogen alone was used, the size of the catalyst had little or no importance and operation could be carried out even at reaction temperature, but as CO or synthesis gas was added there came a time when fluidization would become extremely poor. In these runs one measure of the degree of the success of the particular operation was the amount of synthesis gas ($2 H_2 + 1 CO$) which could be employed and still obtain good fluidization. A wholly successful run from the point of view of fluidization would therefore be an operation in which pure synthesis gas, that is 2 volumes of hydrogen to one volume of CO, was employed under smooth operating conditions. Poor runs were those in which a large volume of extraneous hydrogen had to be added to the synthesis gas in order to obtain fluidization if it was obtained at all. Different sections of the runs will be considered carefully:

<u>A.</u> The operation began with hydrogen alone and 395 pounds of catalyst in the reactor which was maintained at 350°F. and about 16 pounds per square inch pressure. The velocity was 0.23 feet per second and when the operation was stabilized, fluidization was good as indicated by the uniformity of temperature within the reactor. The manometer pressures at each point were stable during the period. The catalyst size distribution at this time was:

0 - 20	μ	21.3%
20 - 40	μ	5.8
40 - 80	μ	9.7
80+	μ	63.2

B. After an hour of steady operation under the conditions described above, synthesis gas was added to the stream to the extent of about 60%. The velocity was now 0.52 feet per second, the temperature went up to 406°F., indicating that reaction had begun, and very poor fluidization was immediately evident by an immediate drop in the Δp over the reactor, (difference between the top and bottom manometer readings) and very rapid surging of the level up and down from 8' to 9.5', whereas in the steady operation under the conditions of "A", the level remained substantially constant at 11'. The temperature during the previous sectional run had not varied more than about 5°F. overall, but under the present conditions wide and rapid variations of 55°F. maximum were found. It was observed that catalyst was being lost from the top of the reactor in excessive amounts. In an attempt to improve the operation, 100% of the synthesis gas was employed, that is without any extraneous hydrogen, but this gave no improvement nor did a change of the velocity to 0.73' per second give any improvement. However, at this point pure hydrogen was again cut in and the steady operating conditions found during period "A" were immediately established. Some catalyst had been lost but the conditions became uniform immediately and fluidization became extremely good again. It was found that about 65 pounds of catalyst had been lost. The velocity was run up to 1.5 feet per second and the conditions remained good. Product was made during the synthesis period but yield was low and appeared to vary from time to time.

C. Switching immediately to 100% synthesis gas, brought an immediate upset of the entire conditions a second time with exactly the same results as referred to before. At this time a portion of catalyst was withdrawn and was found to have the following analysis:

0 - 20	μ	13.4%
20 - 40	μ	6.2
40 - 80	μ	12.7
80+	μ	67.7

D. At this time the amount of catalyst remaining in the reactor was about 230 pounds so that 500 pounds were added and the operation was resumed on pure hydrogen. Fluidization was extremely good and the conditions were about the same as in period "A". Synthesis gas was now slowly added and the amount increased so that it was found that a fair result could be obtained with 42% of synthesis gas and 58% of additional hydrogen. It will be noted that in this case the reactor was operating at only 42% of its nominal capacity. Subsequently continuing the same type of operation showed that the percent of synthesis gas that could be tolerated slowly declined to about 20% and an analysis of the catalyst showed the following:

0 - 20	μ	6.9%
20 - 40	μ	13.8
40 - 80	μ	23.2
80+ -	μ	56.1

It was apparent that the conditions maintaining at this time were not satisfactory and fluidization was progressively becoming poorer.

E. At this point a further volume of catalyst considerably smaller in size than that originally used was added and the analysis now showed.

0 - 20	μ	24.4%
20 - 40	μ	18.1
40 - 80	μ	23.0
80+	μ	34.5

F. After the addition of the catalyst mentioned above, the operation immediately smoothed out without any other changes in temperature and pressure conditions which became quite constant. It was now found possible with the above catalyst to operate with 100% synthesis gas and with a velocity of 1.14 foot per second. The temperature had stabilized at about 425°F. and there was practically no variation from point to point through the reactor. Each of the pressure manometer readings was also maintained substantially constant. During this period the product was collected continuously but due to the low activity of the catalyst the conversion was only about 36%. It was also observed that there was little loss of catalyst during any of this period and that at the end of the period the composition of the catalyst was about the same as before. The unit was operating at its nominal capacity but as stated the conversion was not as high as it should be on account of the poor activity of the catalyst. The operation was much superior to that during any previous period, in other words, the unit was found to be operating mechanically perfectly from the point of view of fluidization. The previous periods had been marked by rapid and wide variation in temperature and pressure fluctuations while in the present period the operation was extremely smooth and quite satisfactory.

Example II.

During the previous runs it had been determined that the size of the catalyst was one of the most important features of the operation so that in the present run a new and active catalyst was employed of the following distribution range:

0 - 20 μ	13.9%
20 - 40 μ	39.9%
40 - 80 μ	37.4%
80+ μ	8.8%

During this run the temperature was held at approximately 400°F. by means of a cooling jacket in place of the cooling tubes used in the reactor in Example I, with little or no variation from point to point in the reactor and 100% of the synthesis gas was fed. As before, this gas comprises 2 volumes of hydrogen, one of CO and a small amount of CO_2. The pressure was 10 pounds per square inch and the velocity in the reactor was varied from time to time from 0.56

to 0.70 foot per second but without any substantial effect on the reaction. During the period measurements were continuously taken over the reactor and the following yields were obtained:

Conversion of CO	86%
Yield cc/cubic meter of gas	162
Selectivity to (C_1 to C_3)	32%
Selectivity to C_4+ (Liquid)	54%

From the above it will be seen that not only was the reactor operating smoothly, but the conversion was high, the yield good and the selectivity fair. The run continued for some 67 hours and there was little loss of catalyst through the entire period. At the 59th hour a sample of the catalyst was withdrawn and it was found to be as follows:

0 - 20 μ	13.5%
20 - 40 μ	38.8
40 - 80 μ	38.0
80+ μ	9.7

This distribution of catalyst is substantially the same as that with which the run was commenced.

<u>Example III.</u>

Apparatus described in Example II was operated with an iron catalyst which had the following characteristics:

0-20 microns	27.8%
20-40 "	24.2%
40-80 "	27.6
80+ "	20.4

After 120 hours reduction with substantially pure hydrogen, synthesis gas was used. During synthesis operation temperatures of about 600°F. and pressures about 300 lbs./sq. in. were employed. The overall gas velocity was about 0.5 feet per second and operation was good. After 119 hours of synthesis operation, catalyst was drawn off and the analysis showed:

0-20	microns	8.5%
20-40	"	28.5
40-80	"	40.0
80+	"	23.0

The height of the catalyst bed was between 20 and 25 feet and the temperatures of the catalyst throughout this length varied only about 10°F.. The pressure manometer readings were smooth and indicated the true weight of catalyst in the reactor which was about 1140 lbs. The heat transfer coefficient, which is a measure of the fluidization, was 44 BTU/Hr.Sq.Ft.°F.

When a coarser iron catalyst was tried in the same apparatus, this heat transfer coefficient at otherwise comparable conditions was only 34 BTU/Hr.Sq. Ft.°F. Furthermore, temperatures varied from point to point in the catalyst bed by as much as 22°F. This coarser type catalyst had the following particle size:

0-20	microns	2.5%
20-40	"	17.8
40-80	"	27.8
80+		51.9

This analysis was made after 82 hours of synthesis operation. These data thus indicate that this coarser catalyst was markedly inferior.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. In a process for producing liquid hydrocarbon materials by reaction of carbon oxides with hydrogen in which a finely divided catalyst is maintained in a vertical reaction zone in a fluidized form and is mechanically separated from the vapor product, the steps of employing a catalyst containing a metal from the group consisting of iron and cobalt and characterized by the following size-frequency distribution:

Micron Diameter	Percent
0 to 20	5% to 25%
20 to 80	30% to 85%
80+	5% to 45%

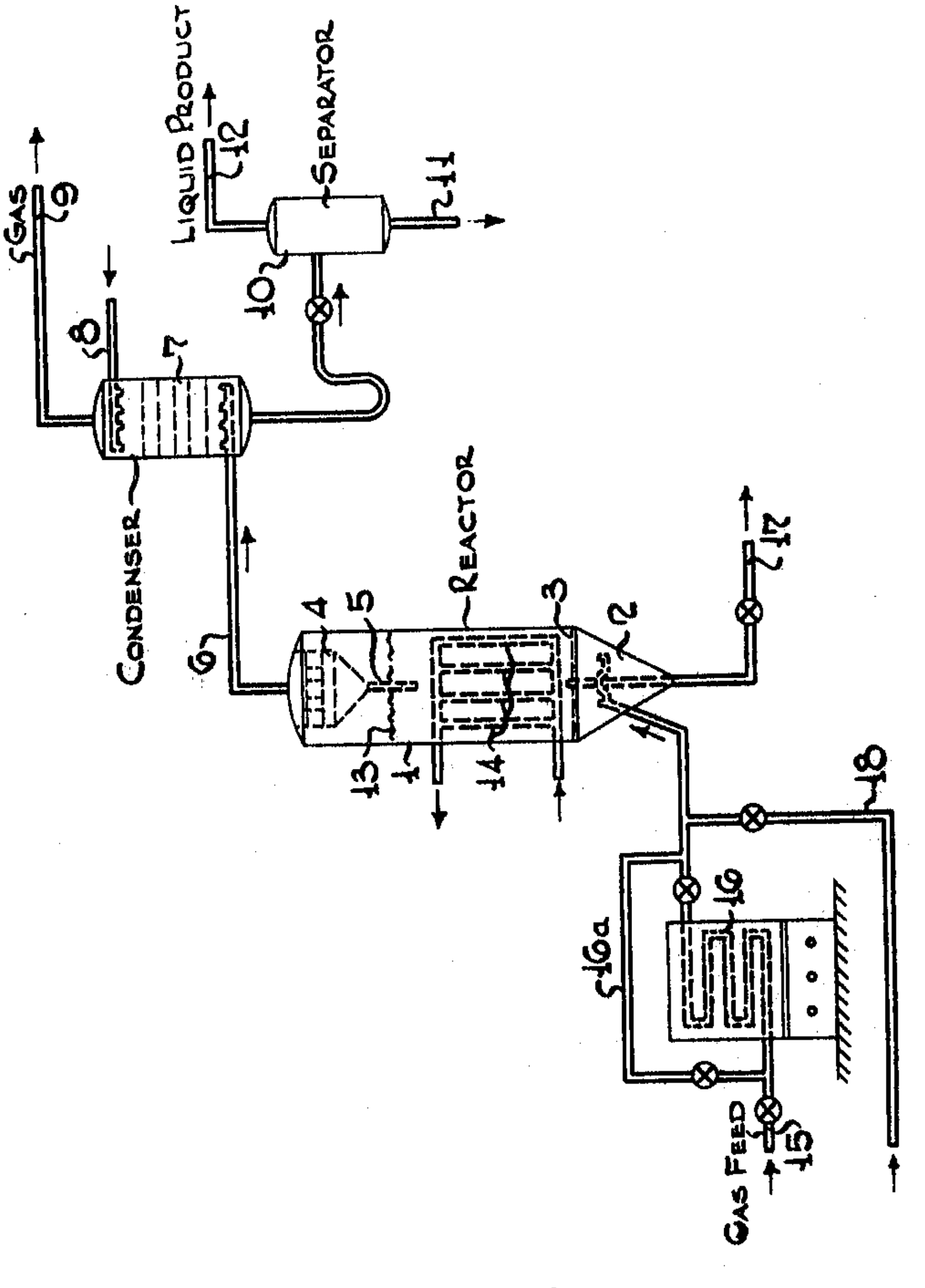
2. In a process for producing liquid hydrocarbon materials by reaction of carbon monoxide and hydrogen in which a finely divided catalyst is maintained in a stable fluidized form within a vertical reaction zone and thereafter the catalyst is separated mechanically from the product vapors, the steps of employing a catalyst containing a metal from the group consisting of iron and cobalt of the following size-frequency distribution:

Micron Diameter	Percent
0 to 20	5% to 25%
20 to 80	30% to 85%
80+	5% to 45%

and maintaining an upward flow of gas through the reactor within the range of 0.2 to 1.5 feet per second.

3. Process according to claim 2 in which the reaction zone is maintained at a temperature from 350 to 650°F.

4. Process according to claim 2 in which the reaction zone is maintained at super-atmospheric pressure 5 to 30 atmospheres.



Certified to be the drawings referred to in the specification hereunto annexed.

Ottawa, Sept. 3 1946

Standard Oil Development Company

Marks & Clerk

A. ORNEYS