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COMPLETE SPECIFICATION

Hydrocarbon Synthesis

We, STANDARD OIL DEVELOPMENT COMPANY, a corporation duly organized and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements in the art of synthesizing hydrocarbons and oxygenated hydrocarbons from synthesis feed gas containing hydrogen and carbon-monoxide and, in particular, it relates to improvements in the art of carrying out such a process employing the fluid catalyst technique.

Heretofore, and prior to the present invention, others have synthesized hydrocarbons and oxygenated hydrocarbons by contacting a mixture containing carbon-monoxide and hydrogen at elevated temperatures and sometimes super atmospheric pressure with a catalytic material in a reactor case containing a fixed or stationary bed or beds of such catalytic material in the form of pills, pellets, granules, etc. Insofar as is known in the earlier work in this field, the catalyst employed was cobalt carried on a support such as Kieselguhr and promoted by an activator such as thoria. After that, it was discovered that iron also in the proper physical and chemical state, was an active catalyst for promoting the foregoing reaction, the temperature, however, required when using the latter catalyst being substantially higher than where the catalyst is cobalt.

And then still a later development in the chemical arts known as the fluid-solids technique was invented and developed commercially in which vapor phase reactions were carried out in the reaction zone containing a bed of fluidized catalyst. Fluidized catalyst signifies a powdered solid catalyst suspended in the vapors or gases to form a dense turbulent ebullient suspension. This type of operation has been used commercially with great success in the catalytic cracking of oil and provides numerous advantages over the older fixed bed type of operation.

The improvements relate to the fluidized catalyst type of operation, and, in particular, to improving the fluidizing characteristics of the catalyst used in synthesizing hydrocarbons.

It is known that certain active and selective iron catalysts employed in the hydrocarbon synthesis are broken down into extremely fine particles in a very short time (25—100 hours) when brought into contact with various mixtures of H_2 and CO employed in the synthesis. Furthermore, the iron in this fine state of subdivision is in its most active form and most selective to liquid hydrocarbons. But in this state it becomes very difficult to fluidise in a fluid catalyst system. It is proposed to dilute the fine catalyst with coarser iron particles having a range of particle diameters between 80—200 microns, depending upon the average particle size of the extremely fine active catalyst. In this manner the average particle size of the mixture can be controlled in the region in which fluidization characteristics are the best. Also the continual breakdown of the larger iron particles caused by the reaction $4CO + 3Fe \text{ - - - } Fe_3O_4 + 4C$ (and also caused by other influences) will serve to replenish the supply of active catalyst as it is lost from the reactor.

In the accompanying drawing, there is shown diagrammatically an apparatus in which a preferred modification of the invention may be carried out into effect.

Referring in detail to the drawing, 1 represents a reactor case which in the illustration shown is a cylindrical vessel having a convex dome and a conical bottom and containing therein a fluidized bed of powdered iron catalyst. This catalyst has a particle size of from 0—200 microns in the fluidizable state, that is to say, when the catalyst will form a dense turbulent suspension having depth from a grid G to a level at say L. In the operation of the process, a mixture of synthesis gas containing hydrogen and carbon monoxide enters the system through line 3 and then is pumped by pump 4 into the bottom of reactor 1 and thereafter passes upwardly through the grid G into the main body of the reactor. By fixing the linear velocity of the gas entering at the point where it is just about to pass through the grid G within the range of from ½ to 1½ ft. sec., preferably about 1 ft./sec., there is formed the dense suspension, or fluidized bed, previously referred to. Depending on the actual number of pounds of catalyst, and the gas velocity, in the reaction zone, the upper level of the dense phase is fixed at L. The distance from G to L may be 20—30 feet. Under conditions which will be more fully set forth hereinafter, the desired reaction takes place and the crude product passes into the space between L and the top of the reactor which may be a matter of 8 or 10 feet. This space is commonly referred to as " a disengaging space " for in it entrained catalyst settles out and gravitates toward the dense phase. The gases and vapors continue upward and are forced through a plurality of solids-gas separating devices M wherein catalyst still entrained in the gases and vapors is separated and permitted to gravitate toward the dense phase through a series of dip pipes D. The gases and vapors containing the desired product, finally exit through the reactor through line 13 and usually these are passed through one or more dust collectors 14 for the purpose of separating the last traces of catalyst. Thereafter, the gases and vapours pass via line 15 into a purification recovery system 16. Since the method of condensing, fractionating and recovering gasoline and similar products is well known, it will not be necessary for us to describe in detail the methods of recovering gasoline, gas or heating oil, etc. present as products in the crude material. The skilled engineer will also understand that in the interest of good practice, it may be necessary to recycle to the reaction zone, unconverted hydrogen, and carbon-monoxide and possibly some of the water and CO_2 formed, the latter being delivered to the reaction zone if necessary to aid in maintaining the catalyst in a fluidized condition.

As has been indicated hereinbefore, the iron of fluidizable particle size tends to disintegrate physically due to the deposition thereon of carbon and carbonaceous material as the reaction proceeds. The undesired results from this catalyst disintegration include the following:

1. Instead of remaining within the reactor, the catalyst passes overhead and exits with the product vapors through line 13. This is true particularly of the catalyst having a particle size less than 20 microns. Obviously this is undesirable because it overloads the cyclones and other solid separating devices and the catalyst appears in large quantities in the condensed liquid products.

2. Poor fluidization causes the finer catalyst particles to appear in greater quantity in the upper portions of the fluidized mass, with the result that a very substantial and undesirable temperature gradient will exist from the bottom to the top of the reactor.

3. Temperature control will be difficult due to improper mixing of the catalyst.

It has been discovered that this condition may be alleviated and corrected by adding coarse catalyst to the reaction zone. Referring again to the drawing, 20 represents the coarse catalyst supply hopper and 21 represents a transfer line in communication with the hopper in the reaction zone. The transfer line 21 is provided with a valve means 22. When it becomes apparent that fluidizing conditions in the reaction zone are poor as evidenced, for example, by a wide temperature difference between the top and the bottom of the fluidizable bed, by the the appearance of unduly large quantities of catalyst fines in the exit line 13, and by rapid rises in temperature in the catalyst bed, coarsely ground catalyst is caused to flow from supply hopper 20 into reactor 1 by operating valve means 22.

In order to explain this invention more fully, there is set forth below in the way of a specific example the operating conditions and the results obtained when employing a powdered iron catalyst in the hydrocarbon synthesis operation, with respect to the effect of physical disintegration of the catalyst as it becomes contaminated with carbonaceous deposits and the means for correcting the fluidizing characteristics of the bed caused by this catalyst disintegration.

EXAMPLE.

In an operation conducted in a fluidized bed of iron catalyst at 650° F. (bed temperature), 400 pounds per square inch pressure, a feed rate of 50 standard cubic feet per hour of hydrogen plus carbon monoxide in fresh feed per pound of carbon and oxygen-free catalyst, 0.8 feet per second superficial velocity of total feed, the following conditions are found:

In Condition A, the particle size distribution of the catalyst is given before the start of the foregoing run; Condition B is the particle size distribution of the catalyst after physical disintegration of the catalyst, resulting in greatly lowered heat transfer coefficient to the cooling surface disposed within the bed; and Condition C sets forth the particle size distribution after 60 per cent by weight of iron having a particle size of from 80 to 200 microns is added. It will be noted that in Condition B the heat transfer coefficient is very low whereas it is restored to nine-tenths of its former value in C by the addition of coarse material.

Roller Analysis (C-free basis)	A	B	C
	Weight Percent		
0—20 microns	11.6	38.2	23.9
20—40	19.8	11.7	7.3
40—80	21.9	33.2	20.7
80—200	46.7	16.9	48.1
Heat Transfer Coefficient BTU/(Hr.) (Sq. Ft.) (°F.)	100	40	90

Not only does the physical disintegration of the catalyst to the point that excessive fines are present (or insufficient coarse material is present) cause poor fluidization but also it causes a lowering of the density of the bed which, like poor fluidization, tends to bring about poor heat transfer and large temperature gradients so that it is desirable from many points of view to maintain the catalyst bed of fluidized iron so that the particle size distribution is such that a major proportion of the particles have a particle size greater than 20 microns and preferably such that there is less than 20 to 25 per cent of fines having a particle size less than 20 microns. When the particle size approaches a condition such that, say, 30 to 40 per cent of the material has a particle size of from 0 to 20 microns, sufficient coarse material (80 to 200 micron size) should be added to maintain the desired particle size distribution. The amount of such coarse material added may be 60% by weight of the total weight of catalyst particles present. It is preferable that a major proportion of the catalyst particles in the reactor should have particle sizes from about 80 to 200 microns.

To recapitulate briefly, methods have been described for improving the fluidization of powdered iron catalyst in the fluid hydrocarbon synthesis reactor. In brief, the improvements involve adding coarse iron to the fluidized bed when it becomes evident that, due to catalyst disintegration, fluidizing conditions are not good therein. It will be appreciated, of course, that in an actual operating commercial plant, the operator will have to exhibit good judgment, and it is impossible herein to predict every possible contingency which may arise with respect to the physical disintegration of catalyst. There is offered by means of specific illustrations sufficient information to teach and guide those skilled in the art, the procedure to be employed in effecting the desired result.

Those who are familiar with this art will realize and appreciate that in operating the so-called fluid catalyst type of operation, a good method is one in which the catalyst may be withdrawn for one purpose or another from the bottom or from the side of the reaction zone—in other words, from the so-called dense phase. These reactors are operated so that there is both a dense phase and a dilute phase in the reaction zone. In other words, the dense phase in a reactor having a diameter, say, of 17 feet (internal) may contain a fluidized dense phase bed of catalyst 20 to 25 feet high and above that a dilute phase in a so-called disengaging space which may have a height of 10 to 15 feet. In the dense phase the catalyst may weigh 125 pounds per cubic foot or more while at the upper portion of the dilute phase, or where the product gases exit from the reactor, the same may, and preferably does, contain only traces of catalyst fines. Furthermore, it should be pointed out that in operating these fluid reactors provision is made for withdrawing samples of catalyst from the dense phase, which catalyst may be analyzed and, in the present instance its carbonaceous content determined in weight per cent, let us say, of the total catalyst. Furthermore, the reactor is provided with a plurality of temperature recording devices such as thermocouples at spaced points in the bed. By the examination of samples and the observation of the temperature prevailing at various levels and, of course, also by the appearance of unduly large quantities of catalyst fines in the gases issuing from the reactor, the operator can observe and record the contamination of the catalyst by carbonaceous deposits, temperature gradients, if any, throughout the bed, and otherwise closely follow the operation of the process. Then, of course, as is well known, there comes a time when it is necessary to withdraw catalyst from the reaction zone for the purpose of regenerating it usually by burning off the carbonaceous contaminants. A good way to restore the activity of the catalyst following the burning of the catalyst contaminants is to resinter the catalyst, that is, to heat it to at least incipient fusion so that agglomeration occurs, at least of the fines, followed by grinding of the catalyst if necessary. Thus, the catalyst with a particle size of from 80 to 200 microns added to the fluidized bed may be either freshly prepared catalyst or previously used regenerated and reground catalyst. As to the catalyst composition itself, the same may be made from spent pyrites by roasting the same to remove sulfur and convert the iron to iron oxide, followed by reduction with hydrogen or some other reducing gas, but preferably hydrogen, and grinding of the catalyst to the proper particle size. Another good catalyst may be made from the iron catalyst used in the synthesis of ammonia from its elements.

In the fluid catalyst process of this invention the preferred temperature within the reaction zone is from 525 to 650° F., and the preferred pressure is from 250 to 700 pounds per square inch.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. In the fluid catalyst process for synthesizing hydrocarbons and oxygenated hydrocarbons from a feed gas containing carbon-monoxide and hydrogen in which the latter are forced into contact in a reaction zone with a fluidized bed of a powdered iron catalyst maintained at elevated temperature and pressure, the improvement which comprises maintaining the bed of catalyst in fluidized condition as evidenced by a high heat transfer coefficient by adding more coarsely ground iron powder to the fluidized bed of catalyst than that contained therein responsive to the tendency of the powdered iron in the fluidized bed to disintegrate physically into particles of smaller particle size.

2. The process as claimed in claims 1 in which the added powdered iron has a particle size of from 80—200 microns.

3. The process as claimed in claims 1 or 2 in which the fluidized mass of catalyst is maintained in such a particle size distribution that at no time does the weight' per cent of the 0 to 20 micron particle size catalyst exceed 20 to 25 per cent.

4. The process as claimed in claim 1 in which, responsive to a drop in the heat transfer coefficient to the fluidized bed of iron, 60 weight per cent of fluidized iron having a particle size of from 80 to 200 microns is added to the fluidized bed of catalyst.

5. The process as claimed in claims 1—4 in which a temperature of from 525° to 650° F. is maintained in the reaction zone and in which a pressure of from 250 to 700 pounds per square inch is also maintained in the reaction zone.

6. In the fluid catalyst process for synthesizing hydrocarbons and oxygenated hydrocarbons from a charging gas containing carbon monoxide and hydrogen wherein the said gas is forced upwardly in a reaction zone containing a bed of fluidized powdered iron, which reaction zone is maintained at elevated temperatures and under elevated pressures, the improvement which comprises adding powdered iron having a particle size of from 80 to 200 microns to the reaction zone as the deposition of carbonaceous deposits on the catalyst occurs during the synthesis to the extent that it causes a physical disintegration of the catalyst, the amount of such powdered iron being such as to maintain the particle size distribution of the total catalyst in the reaction zone such that it does not contain in excess of 20 to 25 weight per cent fines having a particle size of from 0 to 20 microns.

7. The process as claimed in claim 6 in which the particle size distribution of the powdered iron catalyst is such that a major portion thereof has a particle size of from about 80 to 200 microns.

8. The process for synthesizing hydrocarbons and oxygenated hydrocarbons as hereinbefore described with particular reference to the accompanying drawing.

Dated this 2nd day of September, 1947.
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Agent for the Applicants.

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[This Drawing is a reproduction of the Original on a reduced scale.]