PATENT SPECIFICATION

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THE PATENT OFFICE LONDON

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COMPLETE SPECIFICATION

Improvements in or relating to the Synthesis of Hydrocarbons

We, STANDARD OIL DEVELOPMENT COMPANY, a corporation duly organized and existing under the laws of the State of Delaware, United States of America, of Elizabeth, State of New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to improvements in the operation of a hydrocarbon synthesis plant. More particularly, it relates to improvements in the operation of a hydrocarbon synthesis process employing fluidized catalyst technique so that normally liquid hydrocarbons and oxygenated hydrocarbons can be manufactured from carbon monoxide and hydrogen more economically and efficiently than has heretofore been possible.

The synthesis of hydrocarbons from carbon monoxide and hydrogen is a matter of record. The Fischer-Tropsch synthesis for hydrocarbons has been described in patents and other technical literature. A study of this literature reveals that in the early history of this particular art, hydrocarbons were synthesized by contacting them at elevated temperatures with a cobalt-containing catalyst. It shows also that later, iron containing promotional amounts of activators, such as K_2CO_3 was employed as the catalyst and that the temperatures in this later developed process was somewhat higher than in the cobalt process. More recently a great deal of laboratory and pilot plant experimentation has been carried out in this country with the object in view of applying fluid catalyst technique to the hydrocarbon synthesis process. For example, a considerable amount of research work has been and is now being carried out employing powdered iron as a catalyst in the synthesis of hydrocarbons from gaseous mixtures containing carbon monoxide and hydrogen. It has been found that the iron-employing process yields a gasoline fraction of improved anti-detonation quality.

The present invention relates to improvements in the fluidized catalyst technique as applied to hydrocarbon synthesis from carbon monoxide and hydrogen where the catalyst is powdered iron. Research in laboratory and pilot plant operation has revealed that the reaction between carbon monoxide and hydrogen results in the deposition of carbonaceous material on the powdered iron catalyst, and the forces accompanying such deposition cause fragmentation and/or disintegration of the catalyst to particle sizes which cannot be well fluidized. In other words, the synthesis of hydrocarbons as indicated above has presented to the industry problems with which they were not confronted in the development of the catalytic cracking of hydrocarbon oils employing the fluid catalyst technique.

Another problem presented by the application of the fluid solids technique to the hydrocarbon synthesis reaction is the fouling and consequent inactivation of the catalyst by the formation and deposition of waxy materials and the tendency of catalyst particles to agglomerate as a result of the wax formation and deposition. Wax deposition due to catalyst inactivation not only cuts down product yield but causes poor fluidization of the catalyst, poor temperature control, agglomeration of catalyst, and conditions requiring shut down of the plant.

In the course of investigation of the factors that cause wax formation in the hydrocarbon synthesis reaction and the manner in which such formation interferes with fluidization, it has been found that one of the ways wherein wax inter-

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feres with fluidization is by accumulation of wax on any relatively cool walls within the reactor. Fine catalyst particles make contact with this wax, are wetted thereby, and the resulting agglomerate falls into the reactor and causes poor fluidization and/or coking. Thus it has been found that, for example, in a fluid type operation only about 20—25% by weight of wax can be tolerated on the catalyst before it causes sticking together of catalist particles, thus preventing proper aeration and fluidization, which are essential for the operation of the fluid type process. Thus catalyst fines material present in the reactor are conducive to catalyst agglomeration in the manner described above.

It has also been found that catalyst fines are to a great extent, responsible for the formation of wax and wax-like material. Factors promoting formation of these high boiling solids and semi-solids are (a) a high alkali metal salt promoter content, greater than about 1.5% on the catalyst; (b) the state of oxidation of the catalyst, and (c) low heat transfer coefficient. It has been found that the finer catalyst, in size about 0—20 microns, usually contains the highest concentration of promoter, which increases the wax accumulation on this portion of the catalyst. It has also been established that catalyst fines oxidize far more readily and extensively under synthesis conditions than fluidizable particles of larger size; the accumulation of these oxidized fine particles in the reactor causes increased wax formation. Then due to the lower heat transfer coefficients associated with the non-fluidizable fine particles in the reactor, the jacket temperature is usually lowered to maintain a given average temperature. Consequently colder walls are presented to the catalyst and the accumulation of wax on these colder walls and their subsequent return to the fluidized bed as indicated above occurs.

Beside the problem of wax formation, catalyst fines in the fluidized bed have also caused fluidization difficulties. Thus as carbon formation increased and accompanying catalyst disintegration became pronounced, fluidization became increasingly difficult, heat transfer and control increasingly poorer, and plant shut down resulted.

The present invention discloses a method of removing catalyst fines of about 0—20 micron diameter from the dense phase reaction zone as rapidly as they are formed. Hitherto it has been conventional to return to the reaction zone fine sized catalyst entrained from the dense bed by the fluidizing reactants and the vaporous product stream. Thus the entrained stream may be first passed through a disengaging zone wherein the bulk of the entrained catalyst is removed from the gas stream and returned to the dense bed, then passed through a gas-solids separation zone, such as a cyclone filter, electrical precipitator, etc., the fines thus removed being returned to the fluidized bed. This return of fine size particles to the fluid bed, however, though it maintains the catalyst inventory, is accompanied by the disadvantageous results enumerated above.

In accordance with the present invention, however, catalyst fines of a particle size below approximately 20 microns are not returned to the fluidized bed, but are taken overhead entrained in and along with the gaseous fluidizing medium and separated therefrom. The fines, instead of being returned to the dense bed, may advantageously be then sent to a catalyst regenerating zone, wherein the catalyst is regenerated by known processes.

Stated more precisely the present invention provides an improved process for the production of liquid hydrocarbons which comprises feeding a synthesis gas mixture containing hydrogen and carbon monoxide in synthesis proportions into a mass of finely divided iron-containing catalyst in a reaction zone under synthesis conditions of temperature and pressure at such a velocity as to maintain the catalyst in the reaction zone in the form of a dense fluidized bed with a dilute phase thereabove, said velocity being also conducive to the removal from said bed by entrainment of catalyst particles of a size smaller than approximately 20 microns but not conducive to the removal of substantially larger catalyst particles, permitting the mixture of product gases and entrained catalyst fines to flow overhead from the dilute phase in said reaction zone and separating the product gases from the said entrained catalyst fines outside the reaction zone, without thereafter returning the separated catalyst fines to the reaction zone.

The fines entrainment feature of the invention is characterized by numerous advantages. By removing fines from the reaction zone and by preventing their build-up therein by returning them as prior art showed, wax formation is substantially minimized because of the reasons cited. Furthermore, considerably more carbon is associated with fines than there is with coarser fluidized catalyst particles. Thus analyses conducting on catalyst samples withdrawn in the course of a large scale pilot plant run have shown a sharp gradient of carbon content versus the particle size of the catalyst with which the carbon is associated. A roller analysis indicated the following:

Roller Fraction	Percent Carbon		
0—20 Micron	54.8	63.9	61.8
20—40 ,,	6.9	14.1	13.1
40—80 ,,	4.2	5.7	8.1
80+ ,,	3.3	4.4	4.8

By removal of the <20 micron fines and the consequent removal of a substantial part of the carbon from the reactor, the fluid bed density is substantially increased, since carbon has a low fluidized density. The high carbon content of the catalyst fines makes them readily susceptible to oxidative regeneration. The removal of fines from the catalyst bed leaves the latter with substantially higher heat transfer and fluidization characteristics than if the fines were returned and allowed to build up in the dense bed. Furthermore, though it has long been recognized that it is highly desirable to use high gas velocities in the hydrocarbon synthesis reaction in order to increase throughputs and yields, velocities have generally been limited by entrainment considerations. In accordance with the present invention, wherein <20 micron catalyst fines are taken overhead without return as such to the dense bed, these entrainment considerations no longer appear, and thus higher throughput rates and gas velocities may be employed than in the conventional synthesis.

The invention will now be described in more detail by reference to the accompanying drawing which is a diagrammatic representation of a system suitable for carrying out a preferred embodiment of the invention.

Referring now to the drawing, 2 represents a reactor which is preferably in the form of a vertical cylinder having a lower conical section. A synthesis feed gas mixture of hydrogen and carbon monoxide in the ratio of about 0.5—2.0 mols H_2 to 1 mol CO is introduced into reactor 2 through line 4 and flows upward through a screen or grid 10 to effect good gas distribution.

It is generally desirable to remove sulfur compounds and free oxygen from the synthesis gases prior to introduction into the synthesis reactor, and this may be accomplished by any of the processes well known in the art.

Within reactor 2 a mass of iron catalyst, such as sintered reduced pyrites ash, red iron oxide, ammonia synthesis catalyst (fused reduced high purity magnetite containing a small quantity of alumina and potassium promoter), and iron microspheres, is maintained in the form of a powder as such or supported on powdered inert carriers as activated charcoal, silica or alumina having a particle size distribution such that less than 5—10% of the particles have diameters 0—20 microns and less than 60% of the particles have diameters larger than 80 microns. The catalyst is preferably promoted with an alkali metal compound, such as 0.5—1.5% K_2CO_3, Na_2CO_3, KF or NaF.

The superficial velocity of the gases within reactor 2 may be held as high as 0.7 to 1.8 feet per second, although an upper limit of 1.2 to 1.4 feet per second is desirable. It will be understood that lower superficial velocities may be used, satisfactory fluidization ordinarily being obtained as low as 0.3 to 1.0 feet per second, but the high velocity and throughput features and advantages of the invention are not thereby realized. Under these conditions the catalyst in reactor 2 assumes the form of a dense, turbulent mass, resembling a boiling liquid, with a more or less well-defined upper level 3 with a dilute phase thereabove, the dense phase having an apparent density of about 45 to 85 lbs./cu. ft. depending upon the fluidization conditions, the lower apparent densities being associated with the higher velocities. The amount of synthesis gas supplied to reactor 2 is so controlled that about 5 to 30 normal cubic feet of the gas mixture enters reactor 2 per pound iron catalyst per hour, depending on the intrinsic catalyst activity and the operating temperature.

Within reactor 2, the total pressure is maintained in the range of 250 to 750 psig., preferably 250 to 450 psig., and the reaction temperature, which may be controlled by any convenient means, such as a cooling jacket or coil (not shown) inside or outside reactor 2, is kept uniform at about 500° to 750° F., preferably at an upper limit of 650° F.

As heretofore stated, the synthesis gas is passed through reactor 2 at such velocity as to maintain the catalyst in the form of a dense fluidized bed with a dilute phase thereabove. In addition, however, the velocity of the synthesis gas is also such as to be conducive to the entrainment, from the bed, of catalyst particles of a size below 20 microns, catalyst particles substantially larger than 20 microns being retained within the bed. The volatile reaction products and entrained catalyst fines are withdrawn through overhead line 8 and are passed through a conventional gas-solids separator 12, such as a cyclone, filter, or electrical precipitator. This removes the bulk of the entrained catalyst fines from the product vapor stream.

Last traces of catalyst fines may be removed from the product stream by passing the latter through line 14 into oil scrubber 16, wherein the particles not removed in unit 12 are scrubbed in a known manner from the product stream. The latter is then passed to the liquid and gaseous product recovery system for work-up into useful products by any process known *per se*. Recycle gas may be returned to the reactor through recycle line 15.

Catalyst fines separated from the product stream in separator 12 may be withdrawn through line 18, and if desired, may advantageously be sent to a sintering machine 20 wherein the catalyst fines are subjected to sintering temperatures in the range of 1800° to 2500° F. Part of the heat requirements are furnished by the combustion with oxygen or air of the carbonaceous material associated with the fines. The sintered and agglomerated catalyst is then passed to a quenching zone 24, then to grinding zone 26 wherein, in a manner known *per se*, the sintered catalyst may be ground to fluidizable particle size and classified by screening in classifier 27. Catalyst of the desired particle size range may be withdrawn from classifier 27, passed to reducer 28, wherein it is treated with a hydrogen-containing gas, thence discharged through line 30 into a stream of gas containing carbon monoxide and hydrogen where it is formed into a suspension which may then be carried to line 4 and with the feed gas in that line into reactor 2. The utilization of withdrawn catalyst fines by the above sintering process is described and claimed in Specification No. 626,742 to which reference may be made for further details.

The embodiment of the invention as shown in the drawing permits of many modifications apparent to those skilled in the art. Thus mention has not been made of various accessory equipment which normally would be used in a commercial plant. Thus in the interest of good heat economy, various heat exchangers and economizers would be employed to utilize whatever heat is available in the most efficient manner and, in order to control the process, pumps, compressors, valves, flow meters, etc., would be included in the equipment. Also, if desired, catalyst may be withdrawn downwardly from the dense bed for periodic regeneration. Not all the fines withdrawn from the gas-solids separator need be sent to the sintering machine, but may be withdrawn through line 19.

The invention will be further illustrated by the following specific example, which represents a large-scale pilot plant operation wherein a preferred embodiment of the invention was carried out. The plant comprised an 8" reactor section about 17 feet high, and had a capacity of about 100 barrels per day.

To illustrate the improvements resulting from the described invention, comparative data are given in the Table below, wherein two operations are compared in which during A the fines were not removed from the reactor by entrainment and a build-up of fine catalyst and carbon and a decrease in catalyst density in the reactor resulted while in B, when the fine catalyst and carbon were removed by entrainment, the bulk density increased. At the same time, lower temperature differentials existed in the bed and the selectivity to liquid hydrocarbons was greater with the same carbon yield.

TABLE

	A	B
Hours of Operation	289—357	417—429
Temperature, °F.	658	654
Pressure, Psi.	400	395
Feed Rate, V/Hr./W	17	28
Recycle/Fresh Feed Ratio	4.4	4.1
Superficial Velocity F/S	.78	.77
Total Feed Composition		
% H_2	28	20
,, CO	8	8
,, CO_2	31	36
,, H_2O	4.0	1.8
Hydrogen Partial Press., Psi.	116	82
H_2+CO Conversion, %	89	95
Yields, CC, C4+/m3H_2+CO Consumed	158	201
Catalyst* Inspections		
% 0—20 Mu	32	12
,, 20—40 ,,	15	8
,, 40—80 ,,	20	34
,, 80+ ,,	33	46
% Carbon, C+O free, start and end of period	18.7—21.7	15.4—22.7
Density, Lbs./Cu. Ft.	68	90
Temperature Spread in Reactor, °F.	10	6
Carbon Accumulation Rate, Lbs./Carbon/100 Lb. Cat./100 Hrs.	6	5

* Potassium promoted iron powder.

It should also be pointed out that, in order further to improve the operation described above, the hydrogen partial pressure of the feed gas entering the reaction zone should desirably be maintained within the limits of from 125—175 lbs. per square inch. This pressure tends to repress carbon formation in the catalyst and with it fragmentation of the catalyst. This high hydrogen partial pressure is therefore a further and valuable aid in maintaining the catalyst in a fluidizable state for an extended period of time. Also the best operating conditions require a bed density of 40—50 lbs. per cubic foot and after the initial period this may be accomplished by removing fines at the rate of 20—50 per 100 lbs. of catalyst in the reactor every 100 hours. This will remove fines at a rate serving to maintain the bed of catalyst at substantially constant volume and bed density at the superficial velocities hereinbefore disclosed and furthermore since the fines removed contain about 75 parts of carbonaceous deposit per 100 lbs. of the catalyst in which they are deposited, very appreciable quantities of carbonaceous deposits are continuously removed.

What we claim is:—

1. An improved process for the production of liquid hydrocarbons which comprises feeding a synthesis gas mixture containing hydrogen and carbon monoxide in synthesis proportions into a mass of finely divided iron-containing catalyst in a reaction zone under synthesis conditions of temperature and pressure at such a velocity as to maintain the catalyst in the reaction zone in the form of a dense fluidized bed with a dilute phase thereabove, said velocity being also conducive to the removal from said bed by entrainment of catalyst particles of a size smaller than approximately 20 microns but not conducive to the removal of substantially larger catalyst particles, permitting the mixture of product gases and entrained catalyst fines to flow overhead from the dilute phase in said reaction zone and separating the product gases from the said entrained catalyst fines outside the reaction zone, without thereafter returning the separated catalyst fines to the reaction zone.

2. A process according to Claim 1, wherein said withdrawn catalyst fines are subjected in succession to a sintering process whereby they are agglomerated to particles of substantially larger size, and to quenching, grinding, classifying, and reducing processes, the catalyst product from said last-named process being returned to the synthesis reaction zone.

3. A process according to Claim 1 or 2, wherein said velocity is in the range of

0.7 to 1.8 feet/second, and preferably between 1.2 and 1.4 feet/second.

4. A process according to any one of Claims 1—3, wherein the temperature in said reaction zone is in the range of 500° to 750° F., preferably 500° to 650° F., and the pressure is within the range of 250 to 750 pounds per square inch gauge, preferably 250 to 450 pounds per square inch gauge.

5. A process according to any one of the preceding Claims, wherein a hydrogen partial pressure of between 125 and 175 lbs/sq. in. is maintained in the synthesis reaction zone.

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1 SHEET

This drawing is a reproduction of the Original on a reduced scale.