

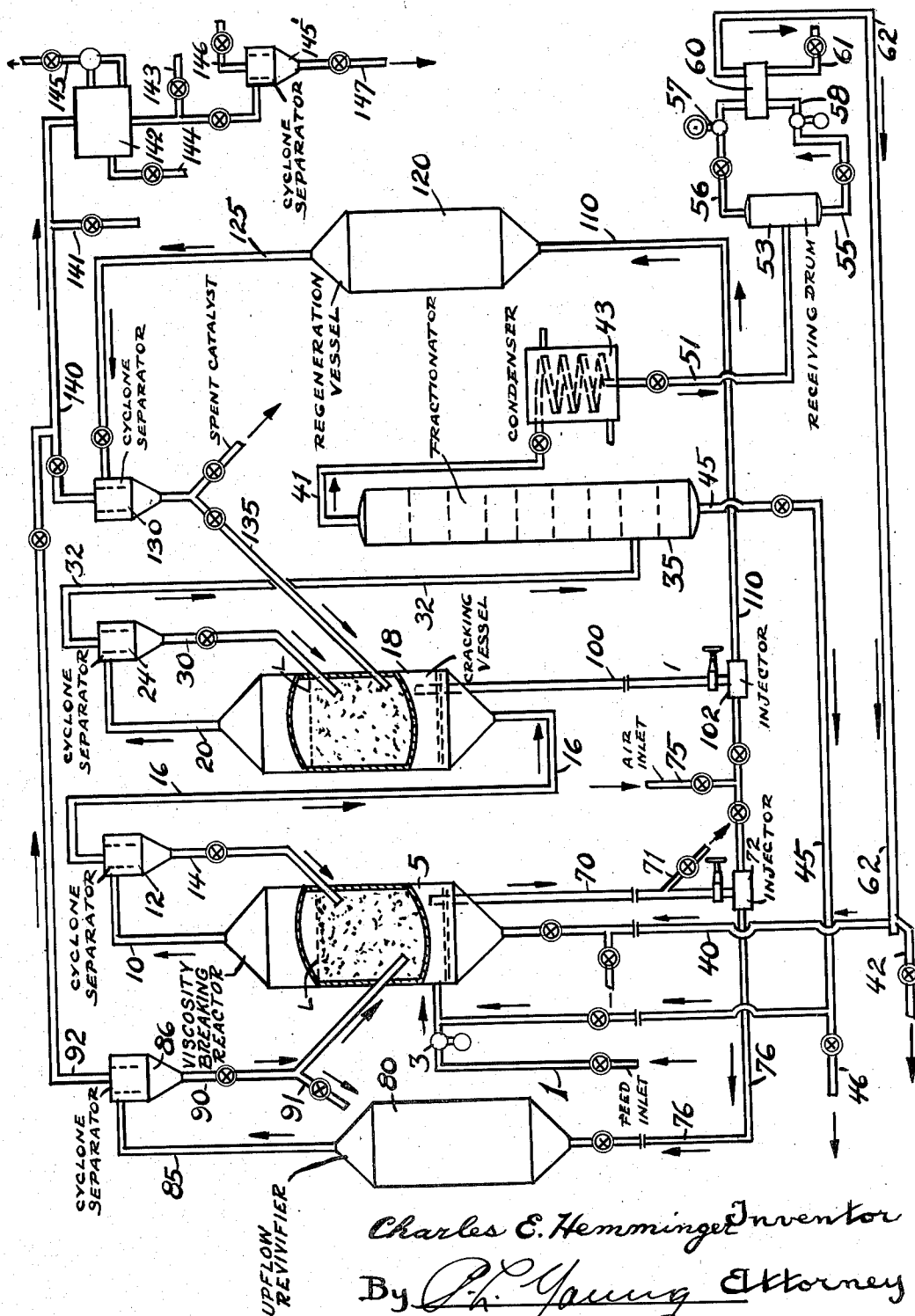
Oct. 30, 1945.

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2,388,055

PETROLEUM CONVERSION PROCESS

Filed June 13, 1942



UNITED STATES PATENT OFFICE

2,388,055

PETROLEUM CONVERSION PROCESS

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Application June 13, 1942, Serial No. 446,850

7 Claims. (Cl. 196—49)

The present invention relates to improvements in the art of treating hydrocarbons and, more particularly, it relates to the preparation of feed stocks for cracking operations.

Prior to my present invention, it has been the practice to subject a heavy hydrocarbon oil such as a reduced crude, to viscosity reducing or to coking in order to convert substantial quantities of the reduced crude to lower boiling fractions, particularly gas oil, which are suitable feed stocks for catalytic cracking or thermal cracking. More recently, however, there have been processes developed for converting reduced crudes or even whole crudes in a single operation to gasoline. In this type of operation the crude is heated up to a temperature of say 900° F. or 1000° F. and then injected in liquid form into a reactor where it contacts a mass of powdered catalyst. In the preferred type of operation, the catalyst is in the form of a fluidized mass or extremely dense suspension and is adapted to be continuously withdrawn from the reactor, regenerated and recycled to the said reactor. When using high catalyst to oil weight ratios and making use of the heat content of the catalyst recovered from the regeneration zone, it is possible to effect the desired conversion of heavy stocks into substantial quantities of gasoline of high octane number, even though the charging heavy oil is merely preheated to temperatures considerably below cracking temperatures and in some cases where the fresh feed is fed into the reaction zone at ordinary atmospheric temperatures. It is obvious that this type of operation presents numerous advantages, since in a one-stage operation gasoline of high octane number is obtained, particularly where the catalyst is an active one such as an acid treated montmorillonite clay or the like, or a synthetic catalyst such as a mixture of silica and alumina or silica and magnesia gels.

In my prior application, Serial No. 363,866, filed November 1, 1940, and entitled "Viscosity reducing," I have described a method for treating heavy stocks in a continuous operation where I inject the heavy oil into a conversion zone where it is converted to hydrocarbons boiling within the gas oil and gasoline ranges, and I have pointed out in said application that where an active cracking catalyst is present in the conversion zone, I obtain a gasoline of improved octane number.

I have now found that in treating some stocks it is not always preferable to convert the heavy stocks in a single stage operation directly to gasoline, but rather it is best to first convert the

heavy oil into substantial quantities of hydrocarbons boiling higher than the gasoline range and then without substantial cooling to conduct the formed gas oil to either a catalytic cracking operation or a thermal cracking operation where the cracking of the gas oil may be effected. I consider it one of the advantages of my present invention, therefore, that by treating the heavy oil in two stages, that is first subjecting it to viscosity reducing and then cracking the formed gas oil in a separate stage, I may more accurately control the actual product of the cracked gasoline so as to improve the quality, the yields, and the product distribution.

One object of my invention therefore is to subject a heavy petroleum hydrocarbon oil, such as a reduced crude to a viscosity reducing operation in a conversion zone where the conversion is carried out continuously in the presence of a powdered material, to recover vapors containing substantial quantities of gas oil from said conversion zone, and then to crack these gas oil vapors without substantial cooling in a separate cracking zone where preferably an active cracking catalyst is present.

It is a further object of my present invention to employ powdered petroleum coke in the viscosity reduction of a heavy petroleum oil in an operation which is conducted continuously since I thereby recover the coke formed in the viscosity breaking and avoid degradation of the charging stock to excessive quantities of coke and improve the overall product distribution to increase the yields of desired constituents, principally gas oil.

It is a still further object of my invention to carry out a combined viscosity reducing operation and a cracking operation under such conditions as to conserve heat.

It is a still further object of my invention to carry out the combined viscosity reduction of a heavy petroleum hydrocarbon oil and cracking of gas oil formed in the viscosity reducing operation in an operation where heat is conserved and other conditions are so adjusted as to make the entire system substantially internally self-sustaining as to heat requirements.

Other and further objects of my invention will appear from the following more detailed description and claims.

In the accompanying drawing, I have shown diagrammatically the combination of apparatus elements in which a preferred modification of my invention may be carried into practical effect.

I shall now set forth in detail a specific example illustrating my invention, with the under-

standing that the precise details hereinafter enumerated are purely illustrative and that it is to be understood that the following details of operation do not impose any limitation on my invention.

In setting forth the said example, I shall refer to the drawing. Referring in detail to the drawing 1 represents a charging line into which a heavy petroleum hydrocarbon oil, such as a reduced East Texas crude oil having an A. P. I. gravity of say about 18°, is introduced into the system and thence pumped by pump 3 directly into a viscosity reducing reactor 5 containing, as will hereinafter more fully appear, a fluidized mass of powdered coke, which coke is in the form of a dense suspension having an upper level substantially at L and being maintained in this condition by a gasiform material which passes through 5 at a slow enough rate to maintain the coke in the fluidized condition referred to. The coke may be maintained in this condition when it is ground to a size of from 100-400 mesh by forcing a gasiform material upwardly through the reactor at a linear velocity of say 0.3-5 ft./second. Under these conditions the coke, as indicated, forms a dense suspension which, however, is not to be confused with the ordinary conception of a suspension which usually means that a solid is suspended in a gas moving at a velocity sufficiently high to cause substantially concurrent movement of solid and gas. In my reactor 5, the velocities are much lower so that there is a slippage of solid with respect to gas, and the final result is that the mass of coke is in a turbulent, ebullient condition resembling roughly a boiling liquid. More details of the manner of injecting the coke in the reactor 5 will be supplied hereinafter. At this point it will merely be pointed out that the coke is preferably maintained at a sufficiently high temperature so that when cold or heated oil is discharged from 1 into the reactor, the oil is heated up to a temperature of 850-1200° F. This temperature may be acquired by maintaining a high weight ratio of coke to oil where the coke is at an inlet temperature of say 1000-1100° F., up to 1300° F. The oil remains resident in the vessel 5, which is maintained under a pressure just sufficient to overcome pressure drops in the subsequent portions of the apparatus and may be of the order of 10-50 lbs. gauge for a sufficient period of time to form vaporized products containing a minimum of gasoline and tar and/or coke, the latter being absorbed by the coke present in the reactor.

The vapors released during the conversion pass upwardly and are withdrawn through line 10 and thence discharged into a cyclone separator 12. The vapors in line 10 contain comparatively small quantities of coke because conditions are so maintained that there is about a 10-20 ft. disengaging space from L to the outlet pipe 10. Therefore, whereas the mass below L may have a density of from say 10-40 lbs./cu. ft., the vapors in line 10 under best operating conditions will have a density of the order of say 0.01 to 0.001 lbs./cu. ft. The fines are separated in cyclone separator 12 and then returned through line 14 to the coking vessel. The overhead vapors, on the other hand, are withdrawn through line 16 and since they are at a temperature of about 850-1200° F. they may be discharged directly into a cracking vessel 18 containing a cracking catalyst also in the form of a dense suspension having an upper level at L', the mass of catalyst being intermixed with the hydrocarbon vapors to form the same

sort of fluidized mass as is present in reaction vessel 5. For example, the catalyst which may be an acid treated clay or a synthetic catalyst such as a mixture of silica and alumina or silica and magnesia gels, or other known catalysts is preferably in the form of a powder having a particle size of from 200-400 mesh, and the flow of vapors upwardly through reaction vessel 18 is so regulated as to linear velocity, that it is somewhere between 0.3-5 ft. per second as to give a dense suspension or turbulent, ebullient mass of catalyst intermixed with the vapors. The heated vapors are in contact with the catalyst for a sufficient period of time to effect the desired conversion which usually is a matter of say 10-15 or 20 seconds, and the reaction products are withdrawn overhead through line 20 and discharged into a cyclone separator 24 where the fines are separated and returned to the reactor through line 30. As before, the vapors in line 20 contain only a very small amount of catalyst if disengaging space between L' and the top of reactor is of the order of 12 ft. even where the density of the mass below L' is as high as from 10-40 lbs. per cu. ft.

In reactor 18, since the total vapors from 5 are reacted therein and since these vapors contain a small quantity of gasoline, as well as a larger quantity of gas oil, the gasoline fraction will be cracked, but this cracking would serve to improve the quality of the gasoline, particularly as regards its octane number. The gasoline produced along with the gas oil will also have a good octane number and finally the normally gaseous products which are present will undergo polymerization and/or isomerization of paraffins, with possibly some alkylation, so that the products withdrawn from cyclone separator 24 through line 32 and subsequently discharged into a fractionator 35 will contain a gasoline fraction of good quality. The vapors in fractionator 35 are fractionated into two fractions, namely, an overhead product which is withdrawn through line 41, passed through a condenser 43, thence withdrawn through line 51 and discharged into receiving drum 53. From receiving drum 53, the lighter hydrocarbons are withdrawn through a line 56 and compressed in a compressor 57 to about 200 lbs./sq. in., or, in other words, sufficiently high to liquefy not only the C₃ but also the C₄ hydrocarbons, or at least a major portion of them. The bottoms from drum 53 are withdrawn through line 55 and these are also pumped into receiving drum 60. The liquid product consisting of gasoline is withdrawn as product through line 61. The overhead from drum 60 is withdrawn through line 62, and this overhead consists essentially of C₃ and lighter hydrocarbons which may be recycled to line 40 to aid in the fluidizing of the solid material in reactor 5, and also to aid in repressing the formation of C₃ and lighter gas from the charging oil during the reaction.

Referring again to viscosity reducing drum 5, coke is continuously withdrawn through the draw-off pipe 70 and preferably is discharged into an injector 72 where it is admixed with air also discharged into said injector through line 75. In the injector 72, a suspension of the powdered coke in air is formed, and this suspension is withdrawn through line 76. Instead of using injector 72 some other suitable mixing device may be employed. The suspension in line 76 is then discharged into a high speed upflow reactor 80, that is to say, it is discharged into a reactor 80 where it flows upwardly at a linear velocity of about

2-10 ft./second, producing a suspension in 80 which is substantially different from that of 5 or 18, in that it is less dense, weighing say from 5-20 lbs./cu. ft. and in which suspension there is much less delayed settling or slippage. In vessel 80, which is in effect a combustion zone, the coke or tar formed in the vessel 5 is burnt, together with some of the original coke, although the amount of the latter which is burnt is preferably limited. Since the coke withdrawn from viscosity reducer 5 is at a temperature of 850-1200° F., the air discharged into the system through line 75 need not be heated to cause active combustion in vessel 80 and the entering air may be at atmospheric temperatures. The revived coke is withdrawn from combustion zone 80 through line 85 and thence discharged into a cyclone separator 86 in which the coke is separated from the flue gases and discharged through line 90 into the coking vessel 5. Flue gases, on the other hand, are withdrawn from cyclone separator 86 through line 92, and these gases may be sent to other dust separators or the like to recover additional coke, but preferably they are discharged directly into a waste heat boiler (discussed later) to recover a portion of their sensible heat.

Due to the viscosity breaking or light pyrolysis of the heavy reduced crude there will be a substantial formation of carbon in reactor 5 on the hot recycled coke. It is the purpose of this invention to build up this carbon on the coke so as to reduce the deposit of coke on the catalyst in vessel 18 and to recover it as a solid carbon. For this purpose powdered coke is withdrawn from the system through line 71 so as to keep the coke inventory in the system constant. After cooling it is a saleable product for a solid fuel, electrodes, carbon bricks and other uses. This coke can also be withdrawn through line 91 from line 90. In the case of line 71 the coke is "wet" because it contains more volatile hydrocarbons than the material from line 90.

Mention should be made that the recovery in the cyclone 12 and auxiliary recovery equipment need not be complete because coke particles passing through line 16 are recovered in vessel 18 and burnt in vessel 120. As such they add heat to the cracking system and by controlling the carbon in line 16 the heat balance in the cracking system may be altered or controlled.

The coke in line 90, due to its passage through combustion zone 80, will normally have its temperature increased a few hundred degrees so that as it re-enters vessel 5 it will have a temperature of 1000-1300° F. or higher. As previously indicated, by using a high ratio of coke to inlet oil, the superheat of the coke will serve to supply the heat necessary in reaction vessel 5, thus tending to make the coking phase of my operation self-sustaining with respect to heat requirements, as is previously indicated.

The catalyst in reaction vessel 18 is continuously withdrawn through line 100 and discharged into an injector 102 where it is mixed with air or some other oxygen-containing gas to form a suspension of catalyst, which is fouled in cracker 18, with air. This suspension is withdrawn through line 110 and thence discharged into a regeneration vessel 120, which is preferably of the high speed upflow type, similar to combustion vessel 80. The catalyst which is at a temperature of about say 850° F. or 1200° F. as it is withdrawn from reaction vessel 18 may be mixed with air, and this mixture when discharged into

vessel 120 will cause combustion of the contaminants on the catalyst to restore the activity of the latter. The suspension will move concurrently upward with respect to air and catalyst, in vessel 120 during the combustion of the said contaminants, and the suspension is then withdrawn through line 125. As in the case of combustion zone 80, the total catalyst is taken off overhead which, as previously indicated, is possible when the suspension moves at a velocity of about 2-10 ft./second where the catalyst is in a particle size of from 100-400 mesh or thereabouts. The suspension is then discharged into cyclone separator 130 where the catalyst is separated from the flue gases and returned to cracker 18 through line 135. This catalyst normally would be at a temperature of 1050-1300° F., as it enters the cracker 18, and here also by using a high catalyst to oil ratio, that is to say, using 5-20 lbs. of catalyst per pound of oil, the cracking reaction taking place in 18 may be fully satisfied as to heat requirements by the sensible heat of the catalyst. Since, of course, in this case the entering oil is not cold and depending on the temperature of the oil vapors in line 16, the amount of catalyst may be reduced and of proportion to maintain the proper temperature level in vessel 18. The flue gases are withdrawn from cyclone separator 130 through line 140, and ordinarily these gases are passed through two or more additional cyclones and/or electrical precipitators to remove the last traces of catalyst, and thereafter the gases may be mixed with the gases in line 92 and sent to some heat recovery system.

The mixing of the flue gases in lines 92 and 140 and the passage to waste heat boiler 142 after introduction of air at line 141, is an important phase of this invention. The potential and sensible heat in these gases are recovered by burning in the boiler 142, giving heat to water introduced through 144 to produce steam in 145, the cooled flue gases leaving through 143. Of course, other uses as for heating oil can be made of this heat in suitable furnaces.

The flue gases in 140 from vessel 120 contain combustibles in the form of CO and slight traces of $H_2 + CH_4$. The CO to CO_2 ratio may be as high as 1 to 1, giving a heat content of about 15 to 25 B. t. u./cu. ft. Due to the low concentration of the combustibles and the low temperature they do not burn in the presence of oxygen and the heat is not recoverable. However, the addition of the hotter gases, usually 50-100° F. hotter, from vessel 80 through line 92 along with the powdered coke and hydrocarbon gases therein makes possible the combustion of the CO from vessel 120.

Another feature of this heat recovery system is that it allows the conversion of part of the coke formed in viscosity breaking in vessel 5 into useful heat in the form of steam. By regulating the recovery of the coke in cyclone 86 and auxiliary equipment, more or less of the coke can be withdrawn from the coke circulatory system. This withdrawn portion is the finer part and as such is a means of regulating the fineness of the coke circulating stream. The withdrawal of this coke also cheapens and simplifies the recovery system 86. In fact, if desired, all of the coke formed in the viscosity breaking can be withdrawn through line 92 and burned to generate steam in boiler 142 as an integral part of the viscosity breaking system.

If desired, a cyclone or other recovery system

may be added 145, 146, 147 after the boiler 142. Then, the combustion in boiler 142 is limited so that unburnt carbon is recovered in cyclone 145'. This carbon will be "dry," that is, contains little volatile hydrocarbons, and as such is a more valuable product than the carbon withdrawn from lines 71 and 91.

It is believed to be obvious that many modifications of my invention will readily suggest themselves to those skilled in this particular art. For example, instead of using petroleum coke in viscosity reducing vessel 5, I may use some other material such as pumice, or I may use an active cracking catalyst such as an acid treated clay, although I prefer to limit the operation taking place in reaction vessel 5 to the production of a maximum quantity of gas oil which I subsequently employ as a feed stock to a cracking operation. With respect to the cracking operation, while I have disclosed a catalytic operation, it will be understood that I may thermally crack the gas oil in cracker 18 at high temperatures in the presence of steam, and by this means secure a gasoline product of improved quality. In this modification of my invention, it is preferable to discharge into cracker 18 1 to 10 or more parts by weight of steam, say at a temperature of 1800-2200° F. per part of oil vapors, in which case I may produce a gasoline of improved octane rating which would make a satisfactory base stock from which aviation fuel may be made by admixing therewith an alkylate, that is, a liquid product produced, for example, by alkylating isobutane with butylene. It will be further understood that the superheat of the flue gases in lines 92 and 140 may be employed to preheat the oil entering the system through line 1, in which case a lesser quantity of hot coke would have to be recirculated to vessel 5 to maintain the viscosity reducing operation.

It will be understood, also, that where I have shown fractionating equipment that the said fractionator is provided with the usual reboiling and refluxing equipment, although they are not specifically shown in the drawing. These details of construction and operation are well known in the art.

While I have shown reactors 5 and 18 to be the "bottom drawoff type," that is, where the bulk of catalyst is drawn off from the bottom through the standpipe, it is to be understood that it is within the scope of my invention to employ reactors where the bulk of the material is withdrawn overhead as, for example, in regenerators 80 and 120; and by the same token, in my invention I may operate regenerators 80 and 120 in the same manner as 5 and 18 are operated, namely, by drawing off the bulk of the powdered material from the bottom of the said regenerator.

It is my intention to claim all of the matter specifically disclosed herein and also that which is inherent by necessary implication, except that excluded by the terms of the appended claims.

What I claim is:

1. The method of producing gasoline from reduced crude petroleum oil in a two-stage operation which comprises first discharging the oil into a heated fluidized mass of powdered coke in a dense suspension, permitting the oil to remain in contact with the said heated coke for a sufficient period of time to effect the formation of substantial quantities of gas oil vapors, withdrawing the gas oil vapors from contact with the coke and discharging them substantially un-

cooled into a fluidized mass of heated cracking catalyst, permitting said vapors to remain in contact with the heated catalyst for a sufficient period of time to convert a substantial portion of the gas oil into gasoline, withdrawing the reaction products from contact with the said catalyst recovering therefrom a gasoline of improved quality and withdrawing both the coke and the catalyst from the viscosity reducing zone and the cracking zone respectively, causing combustion in the presence of air of combustibles associated with the coke and said catalyst in said zones whereby the temperatures of both the coke and the catalyst are increased, and returning the coke and catalyst to the viscosity reducing zone and the cracking zone respectively in sufficient quantity to maintain reactions as regards heat requirements in said zones.

2. A continuous method for producing gasoline from a relatively heavy hydrocarbon oil in a multi-stage operation which comprises discharging the heavy oil into a viscosity reducing zone containing a quantity of subdivided hot powdered coke in the form of a fluidized mass, permitting the oil to remain in contact with the said powdered coke for a sufficient period of time to convert a substantial quantity of said oil into vapors containing gas oil withdrawing said vapors from the viscosity reducing zone and discharging the vapors into a cracking zone containing a cracking catalyst in the form of a fluidized mass, permitting the vapors to remain in contact with said catalyst for a sufficient period of time to effect a substantial conversion to hydrocarbons boiling within the gasoline range, recovering a gasoline of improved octane rating from said cracking zone, reheating the mass of powdered coke by combustion and returning the heated coke uncooled to the viscosity reducing zone in quantities sufficient to supply the heat required for the reaction.

3. The method set forth in claim 2 in which the powdered material in the first-named reaction zone and in the cracking zone are maintained in the form of a dense suspension by causing a gasiform material to flow upwardly in both zones at a linear velocity within the range of about 0.3-5 ft./second.

4. The method set forth in claim 2 in which the powdered material in the first-named reactor and the catalyst in the reaction zone, respectively, are in suspension having a density of about 10-40 lbs. per cu. ft.

5. The continuous production of gasoline from relatively heavy hydrocarbon oils in a multi-stage operation, the improvement which comprises charging the oil into a fluidized, turbulent mass of heated powdered petroleum coke in a viscosity reducing zone, permitting the oil to remain in contact with the heated coke for a sufficient period of time to convert a substantial quantity of the charging oil into gas oil, withdrawing the gas oil as vapors from the viscosity reducing zone and discharging it substantially uncooled into a cracking zone where it contacts a heated powdered cracking catalyst in the form of a dense suspension, permitting the said vapors to remain in contact with said catalyst for a sufficient period of time to effect the desired conversion, withdrawing and recovering gasoline from said cracking zone and maintaining reaction temperatures in both the viscosity reducing zone and the cracking zone by continuously withdrawing powdered coke and powdered catalyst containing carbonaceous deposits from said vis-

cosity reducing zone and said cracking zone, respectively, separately subjecting said petroleum coke and said fouled catalyst to the influence of an oxygen-containing gas at temperatures sufficiently elevated to cause combustion of the carbonaceous contaminants, and thereafter returning substantially uncooled the petroleum coke to the viscosity reducing zone and the regenerated catalyst to the cracking zone.

6. The method set forth in claim 5 in which the powdered coke in the viscosity reducing zone

and the catalyst in the cracking zone are maintained in dense suspension by causing a gasiform material to flow upwardly through said zones at a linear velocity within the range of about 0.3-5 ft./second.

7. The method set forth in claim 5 in which the catalyst to oil ratio is such as to maintain the vapors in the cracking zone at reaction temperatures without the use of extraneous heat.

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