Sept. 23, 1947. C. L. THOMAS 2,427,820

CATALYTIC CRACKING PROCESS

Filed Oct. 27, 1941 2 Sheets-Sheet 1

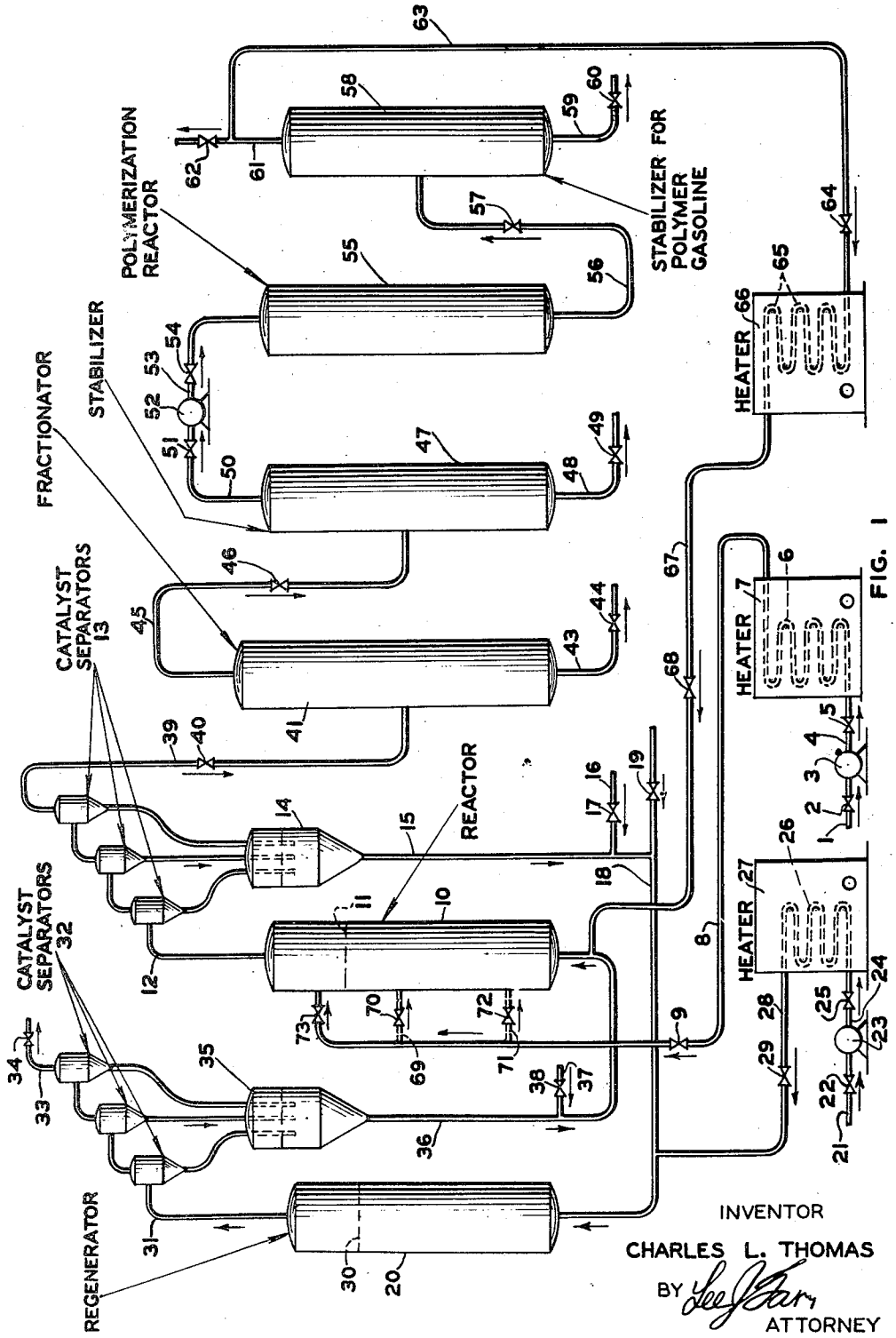


FIG. 1

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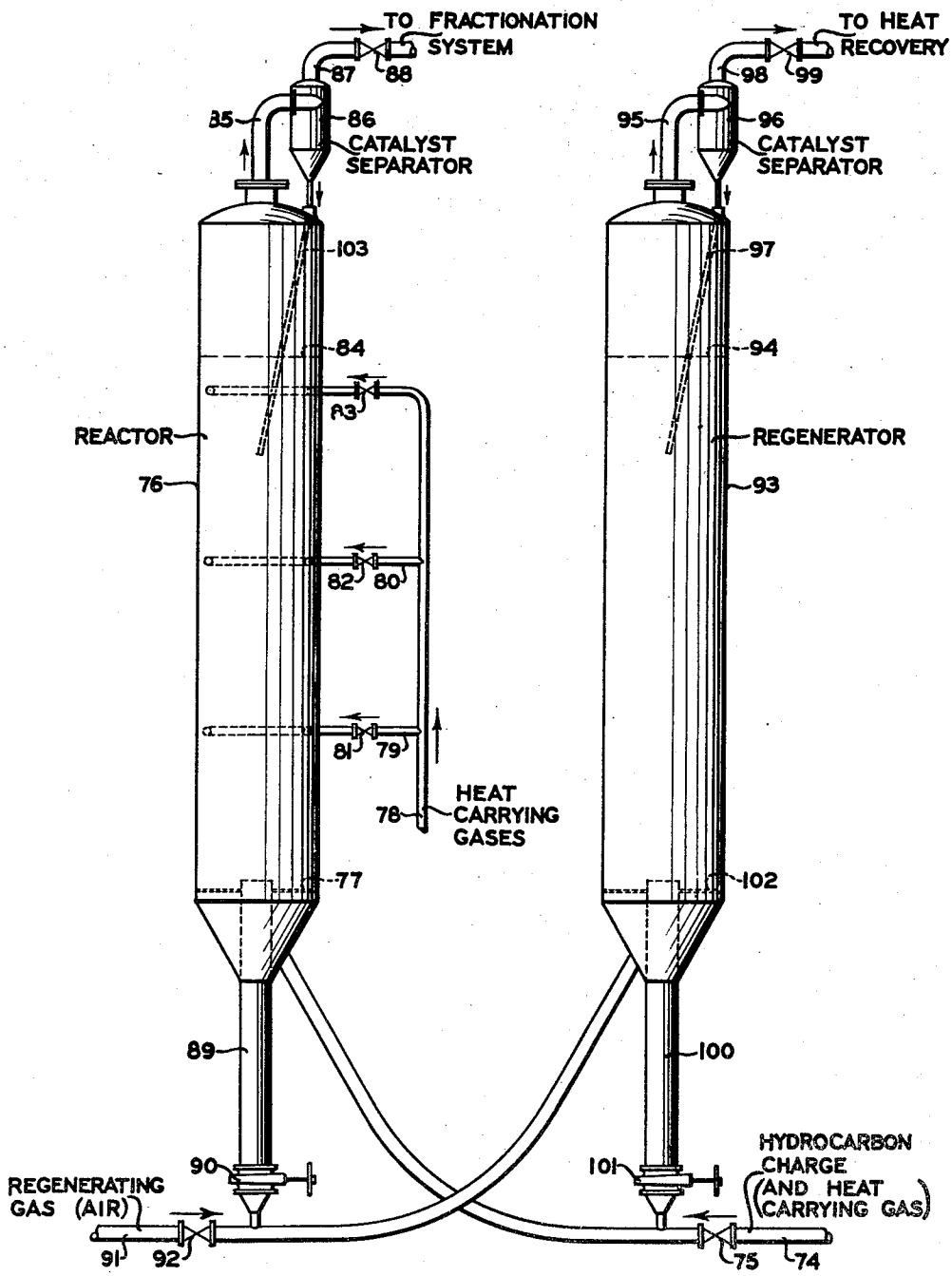


FIG. 2

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CATALYTIC CRACKING PROCESS

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9 Claims. (Cl. 196—52)

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This application relates to a method for the processing of hydrocarbon oils especially those having a high average boiling point. The method is directed particularly to the cracking of heavy hydrocarbon oils such as reduced crudes and other non-distillate petroleum fractions which can not be completely vaporized without excessive deposition of carbon in the heating tubes. The cracking of the aforesaid residual fractions when employing a fixed bed catalyst results in excessively short operating cycles with a subsequent high cost of catalyst regeneration.

My invention also provides a method for the vaporization of such high boiling oils as the aforesaid reduced crudes and other residual petroleum oils. If desired, the vapors could be subsequently catalytically cracked employing either a fixed bed catalyst or a powdered catalyst.

The process of my invention employs a powder which acts as a catalyst if the process is one of cracking or as an absorbent if the process is directed for the vaporization of high boiling hydrocarbons. The charging stock is preheated in a coil under such conditions that usually a portion is vaporized, but by employing temperatures sufficiently low the deposition of carbon in the tubes is prevented or reduced to the usual quantity. The heated oil is then supplied to the catalytic reactor or to the vaporizing zone as the case may be wherein it is sprayed on the powdered catalyst or powdered absorbent depending on the process. The powder is maintained in a fluidized state by the upward flow of preheated gases which may conveniently, in the case of catalytic cracking, be normally gaseous products formed in the cracking operation. If the process is directed primarily toward vaporization, superheated steam might be used instead of the preheated process gases.

In order to describe the process of my invention more clearly, it is illustrated in the accompanying drawings which show in the conventional manner the relationship of the various steps in the process as it is applied to catalytic cracking. Referring now to Fig. 1 of the drawings, the charging stock is supplied to the process by way of line 1 and after passing through valve 2 is directed to pump 3 which discharges through line 4, valve 5 to heating coil 6. If desired a small quantity of catalyst may be added with the charge to the heater thus serving to help keep the heater clean. Heating coil 6 is so disposed as to receive heat from furnace 7, said oil being heated to a temperature which is so controlled as to prevent deposition of carbon in the heating tube. This

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temperature is, in the case of most charging stocks sufficiently great that partial vaporization takes place. The temperature to which the oil may be heated depends considerably on the nature of the charging stock as well as the pressure under which it is heated and on other factors such as furnace design and is of the order of 500–700° F. The heated oil leaves coil 6 to enter line 8 wherein after passing through valve 9 it is supplied to reactor 10, being admitted at a plurality of points after passing through valves 73, 70 and 72 located in lines 8, 69 and 71 respectively. Reactor 10 consists of a vertical cylindrical shell insulated so as to prevent loss of heat to the surroundings and contains a catalyst powder of a density which may be approximately 10 to 20 pounds per cubic foot in the relatively dense phase, the upper level of which is indicated by numeral 11 in the drawing. As hereinbefore set forth the catalyst powder is kept in a state of motion by the flow of heated process gases which supply the heat necessary to vaporize the hydrocarbon charge and to crack the same into lower boiling hydrocarbons. A small quantity of catalyst powder is continuously removed with the heated process gases and the hydrocarbon reaction products by way of line 12 from which it is supplied to a series of catalyst separators 13. The quantity of catalyst suspended in the hydrocarbon vapors varies somewhat with the conditions of operation and in some cases this may be less than .01 pound per cubic foot. The greater portion of this powder is separated in the cyclone separators which discharge into hopper 14 from which it is removed by standpipe 15. In order to insure free movement of the powder in standpipe 15, a small quantity of inert gas such as steam or process gas may be introduced into line 15 by way of line 16, controlled by valve 17. The catalyst powder is discharged from standpipe 15 into line 18 wherein it is admixed with a certain amount of air supplied by way of line 19, the mixture of air and powdered catalyst then being directed to regenerator 20.

The air which may be diluted with inert gases such as spent combustion gases to be used in reactivating the spent catalyst is supplied to the system by way of line 21, controlled by valve 22 from which it is supplied to compressor 23 which discharges through line 24, valve 25 to heating coil 26. This air is heated to a temperature which may be about 850° F. by means of furnace 27 after which it is supplied by way of line 28, valve 29 to line 18 which discharges into regenerator 20. After the unit has been brought on stream

the preheating of the air can be discontinued so that the air is fed to the system at substantially room temperature. The temperature in regenerator 20 may reach a maximum of the order of 1025 to 1050° F. when using an activated clay as a catalyst. If a synthetically prepared composite of silica-alumina or silica-alumina and zirconia is used the regenerating temperature may be somewhat higher and can reach 1300° F. without danger to the catalyst. The flow of air and gaseous products of regeneration maintain the catalyst in a state of constant motion, the surface of the dense phase of the catalyst being indicated by numeral 30. A small quantity of catalyst powder is continuously removed from regenerator 20 along with the gaseous products of regeneration by way of line 31 from which it is supplied to a series of cyclone separators indicated by numeral 32 in the drawing. If desired, the cyclone separators may be followed by a Cottrell precipitator in order to insure complete recovery of the catalyst. The powder free products of regeneration are removed from the system by way of line 33, controlled by valve 34 from which they are directed to steps for recovering their heat content. Methods for heat recovery well known in the art employing waste heat boilers etc. and which are not shown in the drawing may be used. The cyclone separator discharges into hopper 35 from which the regenerated catalyst is returned to the process stage. Standpipe 36 by means of which the regenerated catalyst is returned to the processing reactor may be aerated by means of some gas such as steam or regeneration gases which are introduced by way of line 37, controlled by valve 38.

The hydrocarbon reaction products together with the process gases used as heat carrying medium are directed from the catalyst separators 13 into line 39 from which after passing through valve 40 they are supplied to fractionating column 41. From fractionating column 41 the hydrocarbons boiling above the range of gasoline are separated as a bottoms product, being removed from the system by way of line 42, controlled by valve 43. These higher boiling insufficiently converted hydrocarbons may be returned to catalytic reactor 10 or perhaps more preferably processed in a separate reactor employing either thermal or catalytic methods as may be desired. The overhead product from fractionating column 41 consisting of gasoline boiling range hydrocarbons and normally gaseous products are directed to cooler and condenser, a portion of the condensed product being returned to column 41 for cooling and refluxing. In order to simplify the drawing this condensing step has been omitted as well as the means for returning the reflux to the column. According to the drawing the overhead product from column 41 is directed by way of line 45, valve 46 to stabilizing column 47 wherein gasoline of the proper volatility is separated from the excess quantity of normally gaseous products. This stabilized gasoline is removed from the system by way of line 48, controlled by valve 49. The normally gaseous products separated from stabilizer 47 are then directed to the polymerization reactor. The condensing equipment following stabilizer 47 has also been omitted from the drawing as the operation of a stabilizer is well known in the art and is not claimed as such. The gases separated from the hydrocarbon reaction products are directed to the polymerization reactor by way of line 50, controlled by valve 51, supplying compressor 52 which discharges through line 53, valve 54 into reactor 55 which contains an olefin polymerization catalyst. A catalyst commonly used for the polymerization of olefins consists of phosphoric acid impregnated on some siliceous absorbent such as kieselguhr. Other catalysts for the polymerization of olefins comprise sulfuric acid and copper pyrophosphate.

The mixture of olefin polymers and unreacted paraffins leave polymerization reactor 55 by way of line 56 and after passing through valve 57 is directed to a fractionation step for the separation of the gasoline boiling range olefins from the normally gaseous products. These olefin polymers are removed from stabilizer 58 by way of line 59, controlled by valve 60. Normally gaseous products separated from the olefin polymers are removed from fractionating column 58 by way of line 61 a portion being withdrawn from the system at this point through valve 62. The remainder of the normally gaseous hydrocarbons are reheated and used to supply the heat for the cracking reactor 10 as hereinbefore set forth. This portion of the normally gaseous products is directed from line 61 into line 63 and after passing through valve 64 is supplied to heating coil 65 so disposed as to receive heat from furnace 66. These normally gaseous hydrocarbons may be heated in coil 65 to a temperature of the order of 1000–1100° F. and are directed from coil 65 through line 67, valve 68 into processing reactor 10 as hereinbefore set forth.

Fig. 2 illustrates another embodiment of my invention. It differs from the method described in Fig. 1 principally in the way the catalyst is transferred from the reactor to the regenerator and vice versa. Referring now to Fig. 2 the hydrocarbons leaving heater 6 with or without commingling with a portion of the heat carrying aids, are supplied to line 74 and after passing through valve 75 are commingled with catalysts or absorbent powder leaving the regenerator and the mixture supplied to reactor 76. The lower portion of reactor 76 is equipped with a perforate plate 77 which assists in the uniform distribution of the hydrocarbons in the lower part of the reactor. The hydrocarbon charge flows upward in reactor 76, its vaporization being completed therein and the desired reactions taking place as said hydrocarbons bubble through the relatively dense mass of catalyst powder disposed within the reactor. Heat carrying gases leaving heater 65 now enter line 78 from which they are distributed at a plurality of inlets into reactor 76. As shown in the drawing the heated gases are withdrawn from line 78 by means of line 79 and 80 from which they are directed through valves 81, 82 and 83. As hereinbefore set forth in the discussion of Fig. 1 these hot gases assist in the vaporization of the portion of hydrocarbon charge in liquid state and also supply a portion of heat necessary for the desired chemical reaction in case the process is one of hydrocarbon conversion. The mixture of gases and vapors are disengaged from the dense mass of catalyst the upper level of which is indicated by numeral 84 and leave the upper portion of reactor 76 by way of line 85 from which they are directed to the cyclone separator 86. A plurality of separators may also be used here although only one is indicated in the drawing. The catalyst separated in cyclone separator 86 is returned to the dense phase of the catalyst in reactor 76 by way of conduit 103. The hydrocarbon reaction products

and heat carrying gases leave separator 86 by way of line 87 and after passing through valve 88 are directed to the fractionation system for the separation and recovery of the desired fractions.

The dense mass of catalyst powder in reactor 76 moves downwardly entering conduit 89 from which it passes through flow control valve 90 to enter conduit 91. The regenerating gases which may be pure air are supplied to this conduit and after passing through valve 92 are commingled with the aforesaid contaminated catalyst and the mixture is supplied to regenerator 93. Regenerator 93 has the same general construction as reactor 76 and consists of a vertical cylindrical vessel containing a dense mass of catalyst powder the upper surface of which is indicated by numeral 94. The regenerating gases bubble through this dense mass of catalyst powder oxidizing the carbonaceous material deposited thereon and emerging from the dense mass of catalyst to enter the upper portion of the reactor from which they are supplied to line 95 which discharges into the catalyst separator 96. This separator is of the cyclone type and a plurality of such separators may be used at this point. The catalyst separated from the products of regeneration is returned from separator 96 to the regenerator by means of conduit 97. The products of regeneration substantially free from catalyst leave separator 96 by way of line 98 and after passing through valve 99 are directed to a waste heat boiler, a heat exchanger or other methods for recovering their heat content.

The dense mass of catalyst powder in regenerator 93 flows downwardly entering leg 100 and passes through valve 101 to enter conduit 74 wherein it is commingled with the hydrocarbon charge and returned to reactor 76.

The term gas as used in the specification and claims of this application is to be interpreted in the broad sense, that is, including what are commonly called vapors.

I claim as my invention:

1. A process for cracking relatively heavy hydrocarbon oil which comprises maintaining a mass of finely divided solid cracking catalyst in a reaction zone, introducing a gaseous heat carrying medium to the lower portion of said zone and passing the same upwardly therethrough in contact with the catalyst at sufficient velocity to fluidize the catalyst and form in said zone a lower region of relatively high density and an upper region of relatively low density, simultaneously introducing the heavy oil to be cracked, at least partially in liquid state, to the reaction zone above the point of introduction of the gaseous heat carrying medium, said gaseous medium being introduced at higher temperature than said oil whereby to supply heat for the cracking reaction, retaining the hydrocarbons in contact with the catalyst in the reaction zone for a sufficient time to effect substantial cracking thereof, and removing resultant vaporous conversion products from said zone.

2. A process for cracking relatively heavy hydrocarbon oil which comprises maintaining a mass of finely divided solid cracking catalyst in a reaction zone, introducing a gaseous heat carrying medium to the lower portion of said zone and passing the same upwardly therethrough in contact with the catalyst at sufficient velocity to fluidize the catalyst and form in said zone a lower region of relatively high density and an upper region of relatively low density, simultaneously

introducing the heavy oil to be cracked, at least partially in liquid state, to the reaction zone at a plurality of vertically spaced points above the point of introduction of the gaseous heat carrying medium, said gaseous medium being introduced at higher temperature than said oil whereby to supply heat for the cracking reaction, retaining the hydrocarbons in contact with the catalyst in the reaction zone for a sufficient time to effect substantial cracking thereof, and removing resultant vaporous conversion products from said zone.

3. The process as defined in claim 1 further characterized in that said gaseous medium comprises hydrocarbon gases formed by the cracking of said heavy oil.

4. The method of operating a vapor phase powdered catalyst conversion system which comprises superheating a light hydrocarbon gas to a temperature of at least 1000° F., suspending powdered catalyst as a dense turbulent suspended catalyst phase in a reaction zone by introducing said superheated gas at the base of said zone and separately introducing a charging stock directly into the dense turbulent suspended catalyst phase in the reaction zone whereby the entire conversion is effected while the charging stock is in intimate contact with dense phase catalyst material.

5. The process of converting a reduced crude petroleum residuum into gasoline of high knock rating which process comprises maintaining a mass of solid cracking catalyst of small particle size in a reaction zone, introducing a gaseous heat carrying medium to the lower portion of said zone and passing said gaseous medium upwardly therethrough in contact with the catalyst at sufficient velocity to maintain a dense turbulent suspended catalyst phase in the reaction zone, preheating said residuum to a temperature not substantially exceeding 700° F. under conditions to avoid any substantial amount of cracking whereby said residuum remains largely in the liquid phase, introducing the preheated liquid residuum directly into the dense turbulent suspended catalyst phase in the reaction zone, said gaseous medium being introduced at a higher temperature than said preheated residuum whereby to supply heat for the cracking reaction, contacting said residuum with the catalyst in the reaction zone under conditions for effecting vaporization and substantial cracking thereof accompanied by deposition of carbonaceous material on the catalyst, removing vaporous conversion products from the reaction zone and fractionating said products to obtain a gasoline fraction, a lighter fraction and a heavier fraction, removing catalyst from said reaction zone, regenerating said removed catalyst with an oxygen-containing gas at a higher temperature than the temperature in said reaction zone and returning hot regenerated catalyst to said reaction zone, heating at least a part of said lighter fraction to a temperature higher than the reaction zone temperature and employing it as the gaseous heat carrying medium.

6. The process as defined in claim 1 further characterized in that at least a portion of said heavy oil is introduced to said upper region of relatively low density in the reaction zone.

7. The process as defined in claim 1 further characterized in that at least a portion of said heavy oil is introduced directly to said lower region of relatively high density in the reaction zone.

8. The process as defined in claim 1 further

characterized in that said heavy oil is introduced in part to said upper region of relatively low density and in part to said lower region of relatively high density in the reaction zone.

9. A catalytic cracking process which comprises maintaining a mass of subdivided solid catalyst in a reaction zone, superheating a heat carrier gas to a temperature of at least 1000° F., introducing the superheated gas to the lower portion of said zone and passing the same upwardly through said mass at a velocity such as to maintain a dense turbulent suspended catalyst phase in the reaction zone, separately introducing hydrocarbon charging stock directly into the dense turbulent suspended catalyst phase in the reaction zone, and retaining the charging stock in intimate contact with dense phase catalyst material for a sufficient time to effect the cracking thereof.

CHARLES L. THOMAS.

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