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[54] TWO-STAGE FLUID COKING

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[51] Int. Cl. C10b 47/24, C10b 55/10, C10g 9/32

[58] Field of Search 208/127, 50, 46, 160

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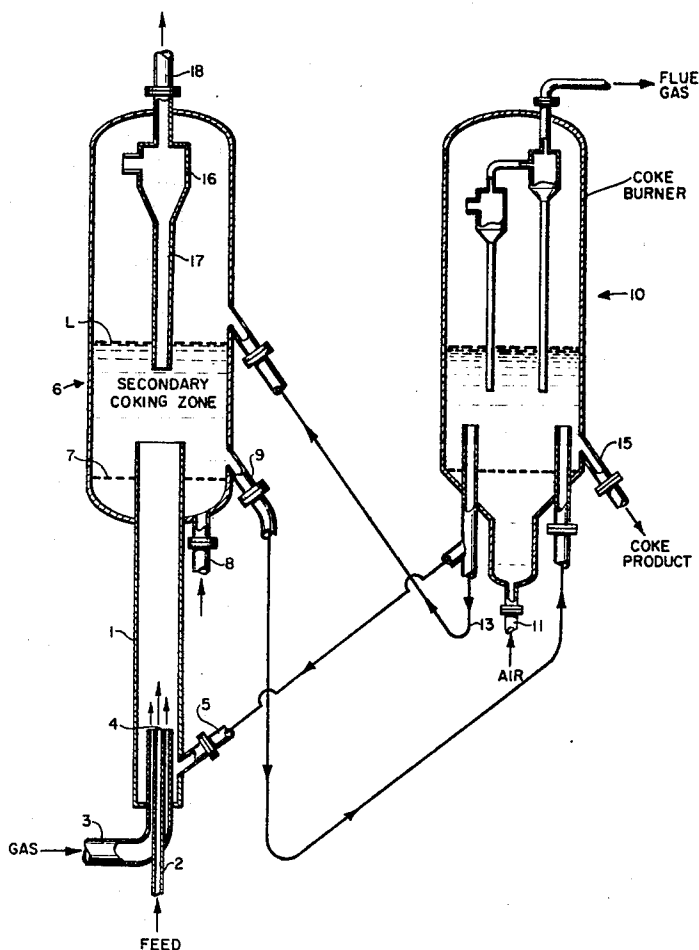
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ABSTRACT

A two-stage fluid coking process in which the first stage is a transfer line for short contact time and the second is either a transfer line or a fluidized bed.

14 Claims, 2 Drawing Figures



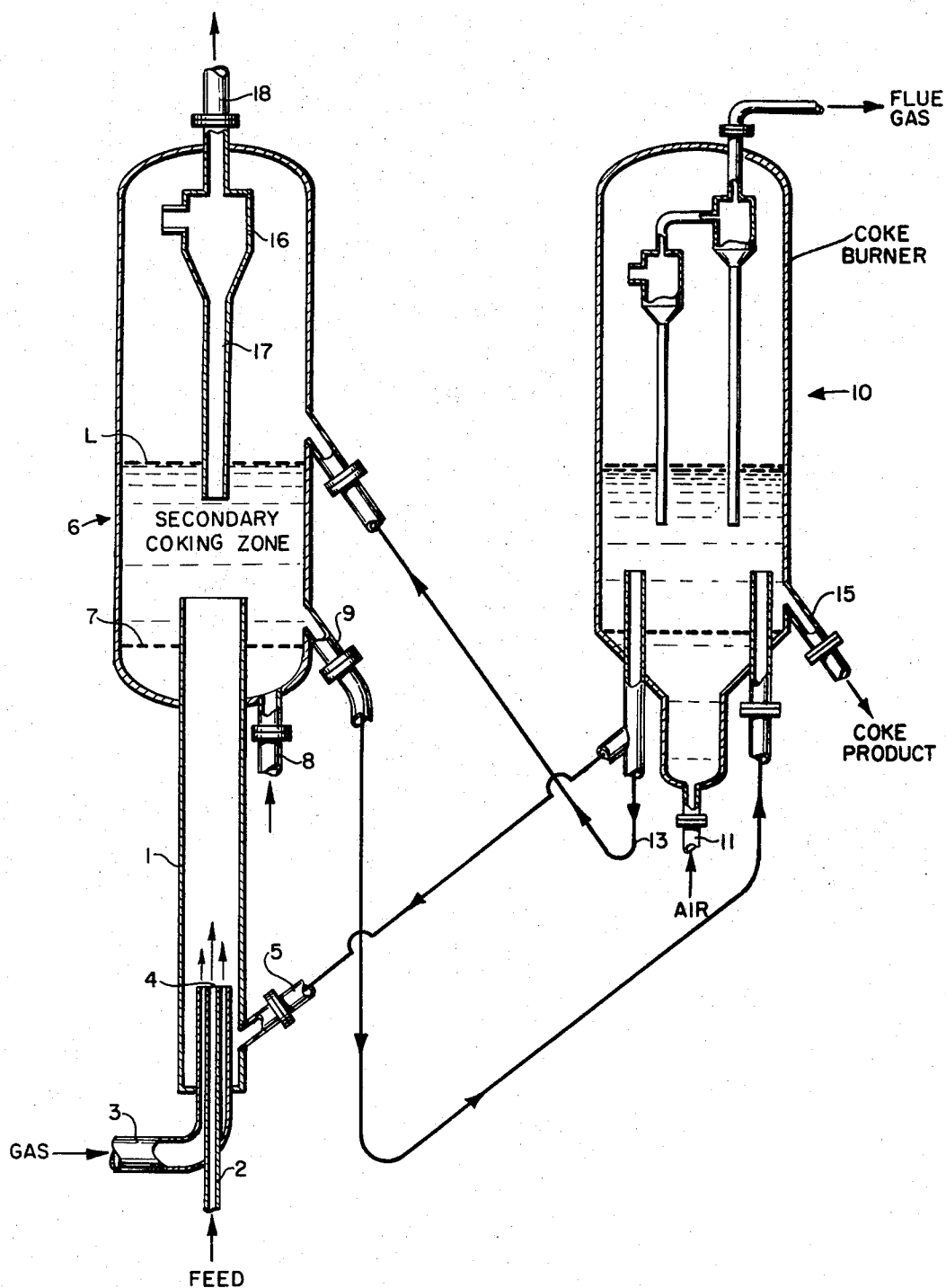


FIG. 1.

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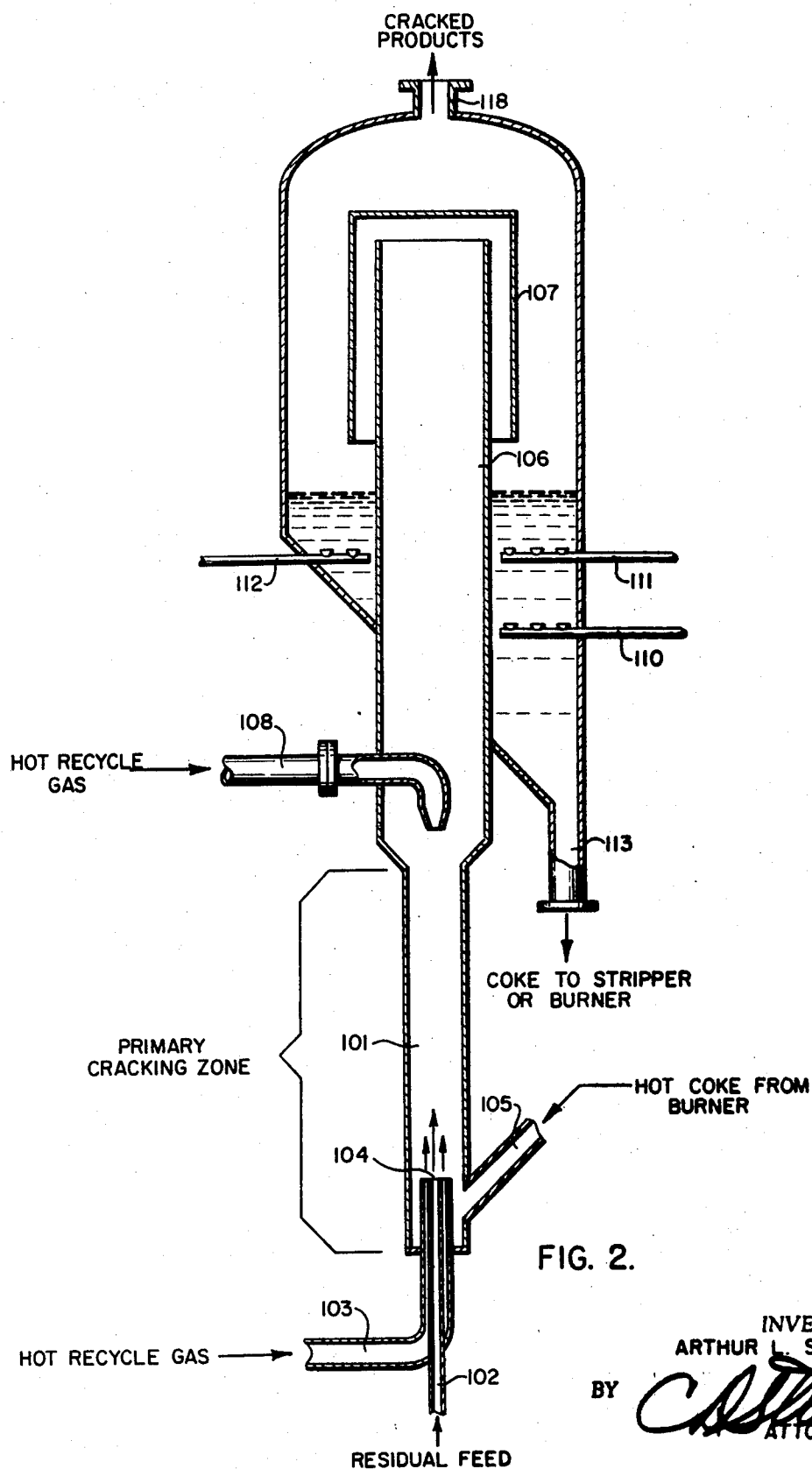


FIG. 2.

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TWO-STAGE FLUID COKING

BACKGROUND OF THE INVENTION

This invention relates to an improved petroleum refining process involving improvements in fluid coking for upgrading of heavy oils. More specifically the invention relates to a method for preventing coke buildup in undesired locations, and—at the same time—providing greater control of product yield distribution.

As is well known in the art, the fluid coking process uses a fluid coking vessel or "reactor" and an external heating vessel, e.g. a fluid bed burner. A fluid bed of solids, preferably coke particles produced by the process having a size in the range of about 40 to 1,000 microns, is maintained in the coking zone by the upward passage of a fluidizing gas, usually steam. The temperature of the bed is maintained at about 950°–1,050° F. by circulating solids (coke) to the heating vessel (coke burner) and back. The heavy mineral oil to be converted is injected into the fluid bed and upon contact with the hot solids undergoes pyrolysis evolving lighter hydrocarbon vapors and depositing coke on the solids. The turbulence of the fluid bed normally results in substantially isothermal conditions and in thorough and rapid distribution of the heavy injected oil. Product vapors, after heavy entrained solids are removed, are withdrawn overhead from the coking vessel and sent to a scrubber and fractionator for cooling and separation. Generally, a stream of the coke particles is continuously withdrawn from the coking vessel or reactor and passed to the burner, where some of it is burned to heat the remainder, and heated coke is continuously recirculated to the reactor.

In such a process many of the operating and maintenance problems are caused by coke formation in unwanted locations, such as feed nozzles, reactor vessel walls, and in the cyclone system. Under normal operating conditions the coke buildup rates are very slow, allowing continuous operations for 18 months or more. However when abnormal operations occur or when coke circulation is temporarily slowed or stopped severe buildups may occur.

Coking of equipment surfaces and particle agglomeration are caused primarily by the high molecular weight fragments produced by very rapid primary cracking of the full residuum feed and by the polymerization products produced by slow secondary reactions including polymerization of some of the primary products and further cracking of other primary products. Coke formation is aggravated in areas where temperature or turbulence are reduced for any reason below critical values.

Present coker reactors must be operated within a relatively narrow range of conditions which limits the degree of control over product yield distribution and over product qualities. This limitation is of relatively minor importance in most current plants where the primary objective is to convert heavy residuum, and the more valuable gaseous and liquid products are a relatively small percentage of the total volume of similar products in the complete refinery. However, improved product flexibility would be a considerable asset to the process, and is particularly important in refineries processing very heavy crudes such that the coker products have a major influence on overall refinery yields.

SUMMARY OF THE INVENTION

The main objects of this invention are to improve the dispersion of hydrocarbon feed in the circulating coke and to separate the reaction system into two zones in which cracking conditions can be adjusted to minimize unwanted coke deposits on the equipment, and to achieve desirable changes in product yields and qualities.

These and other objects are accomplished by providing a two-zone reactor fluid coking system in which the primary cracking reactions take place in a transfer line and the secondary reactions occur either in a second transfer line or in a dense bed into which the primary zone discharges. A high degree of uniform turbulence and independent control over temperature can be accomplished in both cracking zones.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagrammatic representation of one embodiment of the invention involving a two-stage coking process in which the primary zone is a transfer line reactor and the secondary zone is a dense bed of fluidized coke particles.

FIG. 2 is a diagrammatic representation of another embodiment in which both the primary and secondary coking zones are transfer line reactors.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to FIG. 1, a heavy residual oil having a Conradson carbon number generally between 20 and 50 (but not limited to this range) is introduced into the bottom of primary coking zone 1 through line 2 and atomized with about ½ mol of steam or recycled light gases from the process or the like per barrel of feed in line 3 and nozzle 4. Primary coking zone 1 is a transfer line reactor, suitably having a length of 20–40 feet which together with a flow of about 10 lbs. of coke per cubic foot of gas at the bottom to 2.5 lbs. of coke per cubic foot of gas at the top affords a residence of time of 1 to 2 seconds in the primary cracking zone. Hot contact material from a coker burner (described below) is introduced through line 5 and maintains the temperature in the primary reaction zone at about 900°–1,000° F. It should be noted that the above described conditions are illustrative of a representative operation, but are not intended to be restrictive. For example, if a high yield of light olefins is desired, the temperature may be in the range of 1,500° to 1,800° F. with less than 1 second residence time. Alternatively, much higher residence times, up to about 10 seconds may be desired in some cases—for example, for cracking of very refractory materials, such as recycled coker gas oil or other hydrocarbon which has already passed through a prior thermal or catalytic cracking step.

In this example the contact material is coke. However, other materials can be used which may or may not be catalytic in nature. Examples include such commonly used materials as silica, alumina, zirconia, magnesia, combinations of these such as silica-alumina, silica-magnesia, etc. The materials may be synthetically prepared or may be naturally occurring materials such as pumice, clays, kieselguhr, diatomaceous earth, bauxite, and the like. When it is desired to use a contact material having catalytic properties the material will generally comprise silica-magnesia or other catalytically active combinations of inorganic oxides and when it is desired that hydrogenation activity be imparted to the catalyst other material may be added such as small quantities of metals having hydrogenating activity including nickel, cobalt, iron, molybdenum, vanadium, chromium, platinum, palladium, etc., compounds of these such as their oxides or sulfides or any combinations thereof. Since no net coke make need be realized, a heterogeneous contact material comprising a refractory oxide base stable at the high temperature herein contemplated may be used.

The contact of the residua and hot contact material results in the pitch being converted to coke which deposits as thin layers on the hot particles, and lower boiling hydrocarbons which pass overhead in the vapor state. The reactions occurring can be grouped in two general classes. First there is the very rapid primary cracking of the full residuum range to form a broad spectrum of products from H₂ and CH₄ to very high molecular weight fragments. These will include large amounts of unsaturated and unstable compounds as well as some very refractory materials. Second there are the slow secondary reactions including polymerization of some of the primary products and further cracking of other primary products. These secondary reactions are held in check somewhat by the relatively low temperature and short residence time in the primary reactor thus minimizing coke formation since coking of the equipment surfaces and particle agglomeration are caused primarily by the high molecular weight fragments from the primary cracking and subsequent polymerization of the products from the secondary reactions. Coke deposition on equipment

surfaces is further minimized by the scouring action of the particles which are carried up in a suspended state at velocities ranging from about 10 to 40 ft/sec.

In any case the contact of the residuum and the hot contact material results in the residuum being converted to coke and lower-boiling vaporous hydrocarbons.

The primary coking zone 1 discharges into the bottom of secondary coking zone 6 containing a dense fluidized mass of particles of contact material having a level L, and resting on distributing grid 7 through which hot fluidizing gas is distributed and which is introduced into the bottom of the secondary zone below the grid 7 through line 8. This fluidizing gas may suitably be hot recycle gas from the processes, steam, or any other suitable fluidizing gas. This gas serves several functions: it assures good fluidization thereby minimizing temperature gradients which could lead to coke deposits in cool zones; it provides a means of controlling the gas atmosphere and thereby influencing product yields from cracking; it also serves to add heat to this zone. The temperature of this secondary zone is preferably slightly higher than that in the primary zone, namely, about 920°–1,050° F. and the residence time is typically 1 to 10 seconds.

A stream of fluidized coke is transferred from secondary zone 6 through line 9 to a coke burner 10 where a portion of the deposited coke layer is burned to generate heat for the process. A conventional countercurrent stripper (not shown) may be provided to remove any strippable hydrocarbon from the coke leaving the secondary coking zone. Combustion air is supplied through line 11. Heat is returned to the reactor in a recycled coke stream (lines 5 and 13) which is normally about 100° to 200° hotter than the coke stream from the reactor to the burner. The recycled coke temperature, which equals the burner bed temperature, is normally controlled by regulating the quantity of combustion air. The relative quantities of recycled coke through line 5 to the primary cracking zone and through line 13 to the secondary cracking zone are regulated as required to maintain the desired cracking temperatures in the two zones. Another consideration affecting the distribution of recycled coke to the 2 cracking zones is the ratio of particle surface area to residuum feed in the primary zone. The particle surface must be sufficient that the atomized liquid residuum feed can be distributed in a thin film over the surface, thus avoiding excessive agglomeration of particles in large liquid droplets. In a normal case this is not a limiting consideration relative to the mass flow rate of particles required to supply the reaction heat. Typically, the mass flow ratio of hot coke to residuum feed will be in the range of 3/1 to 10/1.

The net coke product, which equals the gross coke deposited on the particles in the reactor minus the coke burned in the burner, is withdrawn from the burner through line 15.

Vaporous products and entrained solid particles pass from the upper portion of secondary coking zone 7 into cyclone separator 16 where solid particles are separated and drop into the fluidized bed through line 17. Vapors leave through line 18.

Referring now to FIG. 2, primary cracking zone 101 is identical with the primary zone of FIG. 1 and operates in the same manner. Instead of discharging into a dense fluidized bed in a secondary coking zone as in FIG. 1, it discharges into a transfer zone 106 which is slightly longer than transfer line 101 so as to increase the residence time. Typically transfer zone 106 will provide from 1 to 5 seconds residence time. Hot recycle gas is introduced into the bottom of this zone through line 108 to add heat and to control the reaction time and the atmosphere in which cracking occurs. The mixture of coke laden contact particles and gas discharge from secondary zone 106 against deflecting hood 107 and fall into dense bed 109 which is maintained in a fluidized state by hot recycle gas or other fluidization and stripping gas introduced through lines 110, 111 and 112. Hot coke-laden particles are withdrawn from the bottom of fluidized bed 109 through line 113 and passed to a burner (not shown) which is identical with the

burner 10 of FIG. 1. Cracked products are withdrawn overhead through line 118.

From the above description it is evident that an improved coking and cracking process has been developed which minimizes deposition of coke on equipment surfaces, prevents "boggling" or excessive agglomeration of sticky particles, and gives improved yields of products. The system will have more uniform and predictable fluidization characteristics than conventional single stage coker reactors which will result in improved operability. The particle size of the circulating coke can be allowed to increase which will reduce or eliminate the need for forced attrition. Present plants utilize steam jet attriters as a supplement to normal attrition within the system—to generate "seed coke" particles which replace the particles withdrawn as product or blown overhead, and to reduce particle size for operability reasons.

The conditions described in the above example are typical of an operation in which the primary objective is to obtain a maximum yield of liquid products from a residuum feed. Other hydrocarbon feeds can be processed and conditions can be varied widely, within the scope of this invention, to accomplish widely different yield patterns. For example, the reactor can be operated at 1,500° to 1,800°, with a correspondingly higher burner temperature, to maximize the yield of H₂ and light hydrocarbon gases. The yield of "unsaturated" compounds can be maximized by a combination of elevated temperatures and steam dilution as injection and fluidizing steam. Use of H₂ rich gas for injection and fluidization will minimize the dehydrogenation of gaseous and liquid products, thereby, yielding maximum "saturated" products.

The process described can be operated over a wide range of pressure. The most normal pressure is from about 15 to 50 psig. However, it is well known that operating pressure is an important parameter affecting cracking process results. Operating pressure also affects physical equipment sizing and overall economics. Thus, in particular situations, it may be desirable to design a two-stage fluid coking system as described herein, for operations at elevated pressures in the range of 200–300 psig.

The present invention having thus been fully described and illustrated, what is claimed as new, useful and unobvious and desired to be secured by Letters Patent is:

1. A process for cracking heavy hydrocarbon material to coke and lighter gaseous and liquid hydrocarbon products, which comprises:

contacting said heavy hydrocarbon material with hot particulate solids in a first reaction zone operating at cracking pressures and temperatures to produce said lighter products, said contacting being for a period of the time to enable cracking of said heavy hydrocarbon material to occur under said cracking pressures and temperatures, but not for a period of time to enable substantial amounts of coking and particle agglomeration within said first reaction zone;

passing said hydrocarbon material that is not cracked in said first reaction zone, said hot particulate solids, said lighter products and coke into a second reaction zone operating under cracking conditions more severe than in said first reaction zone to enable more of said hydrocarbon material to be cracked to more lighter products; and recovering said lighter products from said second reaction zone.

2. A process according to claim 1 wherein said cracking conditions in said second reaction zone is more severe than in said first reaction zone in that said cracking temperature in said second reaction zone is higher than in said first reaction zone.

3. A process according to claim 2 wherein said cracking temperature in said second reaction zone is between about 20° and about 50° F. higher than in said first reaction zone.

4. A process according to claim 1 wherein a portion of said heavy hydrocarbon material is atomized before contacting with said hot particulate solids.

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5. A process according to claim 4 wherein said heavy hydrocarbon material is atomized by contacting with a stream of steam or recycled light gaseous products which have been recovered from said second reaction zone.

6. A process according to claim 5 wherein said atomizing and contacting occur simultaneously in said first reaction zone.

7. A process according to claim 6 wherein said oil is atomized by contacting with a stream of steam or recycled light gaseous products which have been recovered from said second reaction zone.

8. A process for cracking a heavy residual oil having a Conradson carbon number generally between 20 and 50 to form coke and lighter gaseous and liquid hydrocarbon products, which comprises:

contacting said oil with hot particulate solids in a first reaction zone operating at a cracking temperature between about 900° and about 1,000° F. and at a cracking temperature between about 15 and about 50 psig to produce said lighter products, said contacting being for a period of time between about 0.5 and about 10 seconds;

passing said remaining oil, said hot particulate solids, said lighter products and coke into a second reaction zone operating under cracking conditions more severe than in said first reaction zone to enable more of said oil to be

cracked to more lighter products; and recovering said lighter products from said second reaction zone.

9. A process according to claim 8 wherein a portion of said oil is atomized before contacting with said hot particulate solids in said first reaction zone.

10. A process according to claim 8 wherein a portion of said oil is atomized simultaneously with said contacting in said first reaction zone.

11. A process according to claim 8 wherein said contacting in said first reaction zone which is a transfer line reactor being for a period of time between about 1 and about 2 seconds.

12. A process according to claim 11 wherein said second reaction zone is a transfer line reactor, and said oil is contacted with said hot particulate particles for a period of time between about 1 and about 5 seconds.

13. A process according to claim 8 wherein said cracking conditions in said second reaction zone is more severe than in said first reaction zone in that said cracking temperature in said second reaction zone is higher than in said first reaction zone.

14. A process according to claim 13 wherein said cracking temperature in said second reaction zone is between about 20° and about 50° F. higher than in said first reaction zone.

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