D. D. MACLAREN

DUAL ZONE FLUID COKING PROCESS

Filed Feb. 15, 1957

Donald D. MacLaren    Inventor

By K. Chasan    Attorney
The present invention relates to an improved process for converting heavy hydrocarbon oils into desirable lower boiling products. More particularly, it deals with a process in which the product distribution of a thermal cracking operation is improved while utilizing a relatively simple reaction system. Specifically, it contemplates the use of large size catalytic solids as a means for both supplying heat to the conversion process and enhancing yields of more valuable products.

The desire for improving the efficiency and selectivity of converting heavy oils such as residua, crudes, asphalts and the like, to give high yields of valuable lighter products has long been felt in the art. While direct catalytic cracking of the heavy oil has been proposed in the past, such an operation has been found to suffer from numerous difficulties. Heavier feed components tend to contaminate the catalyst particles by depositing metallic materials such as nickel or vanadium on their surfaces, thereby reducing their intrinsic activity and degrading their selectivity. Approximately one-fourth of the oil feed is converted to coke, the coke depositing on the surface of catalytic solids. In order to oxidize this large amount of coke, considerable quantities of oxidizing gas must be supplied to the regenerator, thus necessitating the use of expensive gas compression equipment. Further, the heat released in the regeneration is greatly in excess of that necessary to maintain the conversion system in thermal balance, and regenerator cooling coils are needed. Summarily, direct catalytic cracking of heavy oil feeds is too expensive a process to justify the increase in product values.

In an effort to solve the problem of treating such heavy oil feeds, the fluid coking process has been developed. In this process, the hydrocarbon oil is injected into a dense, fluidized mass of inert particles maintained at a temperature suitable for converting the feed to lighter vaporous products and coke, the coke normally depositing on the bed particles. The contact solids are usually coke granules averaging 40 to 400 microns in size, although sand, ceramics, glass beads and the like may be readily employed. Generally, about 25% of the coke thus formed is withdrawn in the form of coating on the surface of the contact solids, burned in a burner zone, and the solids are returned to the system, a relatively simple burner vessel with a minimum of extraneous equipment may be employed.

However, in order to realize the advantages of the use of heat control, and relatively inexpensive mode of operation characteristic of the fluid coking process, one sacrifice has to be made in the product distribution obtained. Compared with a reaction in a fresh bed of catalytic solids, the fluid coking process produces lower valued products in terms of poorer quality gasoline, and lower yields of middle distillates and gas oil. The present invention provides a means for obtaining the benefits of a fluid coking operation while improving the distribution of the products obtained.

More specifically, according to the present invention, large size catalytic solids are employed in a fluid coking reaction bed. The catalytic solids, readily separable from inert bed particles in response to the force of gravity, are circulated to a burner zone wherein oxidation of carbonaceous deposits serve to impart sufficient heat to the particles to enable them to supply the thermal requirements of the cracking reaction. By adjusting the relative amounts and sizes of catalyst and inert solids, the quantity of coke deposited on the catalytic particles is approximately that required for oxidation to supply heat for the overall process. A portion of the circulating catalyst is treated in an attrition zone to remove contoured surface layers, thus maintaining a relatively active and selective catalytic level in the reactor. The remaining coke produced is simply withdrawn as product in the form of coated, inert solids as is normally done in fluid coking operations. Hence, improved yields due to the presence of catalysts are realized while employing essentially the same operations and equipment as found in conventional fluid coking.

By way of clarifying nomenclature, it should be understood that the term "catalytic shot" is used to denote the large sized catalytic particles of the present invention. The expression "feed solids" refers to the inventory of small sized inert particles, normally necessary in a fluid coking reaction to maintain average bed solids' size sufficiently small so as to prevent excessive bogging and loss of fluidity.

The present invention will be more clearly understood by referring to the following description, drawing and accompanying examples.

The drawing, illustrating a preferred embodiment of the present process, depicts a conversion system consisting essentially of reactor 1 and heater 2. A relatively dense turbulent conversion bed 3 is maintained in reactor 1 at a temperature of about 950°F. The bed is composed primarily of coke particles averaging 40 to 400 microns in size, although other suitable inert solids may be readily employed. Admixed with the coke particles are large sized catalytic solids, such as silica-alumina cracking catalyst, generally ranging between 1000 and 4000, preferably 2000 to 2500, microns in size. Other conventional cracking catalysts such as activated clay, silica-magnesia, or mixtures thereof, may be alternatively utilized. A supply of these catalytic shot particles is continuously circulated to reactor 1 from heater vessel 2 by means of line 22 at a catalyst to oil weight ratio of about 8 to 9. The catalysts enter the reactor at a temperature of about 1100°F. At these conditions the catalytic shot supplies requisite thermal energy for the conversion of the oil feed. The catalytic particles are preferably introduced into the lower portion of bed 3, thereby providing a space velocity of about 12 to 20 wt. of feed/hr./wt. of catalyst based on total reactor feed, about 3 to 5 wt./hr./wt. based on the portion of the feed which the shot catalyst contacts while settling.

A heavy hydrocarbon oil feed such as a West Texas 1100°F. 9°-residuum, preheated to a temperature of about 700°F., passes from line 4 into multiple feed nozzle 5 whencefrom it is injected into fluidized bed 3. Upon contact with the hot mixture of inert and catalytic solids, the oil feed is converted into lighter vaporous products and carbonaceous material. Gaseous products, unconverted vaporized feed and fluidizing steam, supplied at an overall rate of 5 to 15 wt. percent based on feed by means of line 10 and jets 11, 12, and 32, as will be.
further described, pass upwardly from the conversion bed and are withdrawn overhead. Entrained solids are removed in cyclone-separator 6, and returned to the conversion zone by means of dipleg 7, generally extending below plane of bed 3. The gases withdrawn through conduit 8 are then sent to further product recovery treatments, not shown. Generally the gases undergo scrubbing, fractionation, and other conventional processing steps, to recover product streams of gasoline, light and heavy gas oils and other valuable materials. A significant amount of the oil feed is converted to coke, approximately one-fourth of which is deposited on the surface of the large size shot catalyst, the remaining portion coating the inert contact solids. Shot catalysts, thus coated with carbon, settles downwardly to form bed 9 in the lower portion of the reactor. Fluidizing steam is advantageously supplied upwardly through bed 9 by means of line 10 for a number of reasons. First, it serves to strip coke particles from between the large catalytic shot particles. Second, it strips declined hydrocarbons from the catalyst particles. Third, the steam is substantially uniformly distributed in the lower portion of the reactor prior to fluidizing the reaction zone. Coke product, i.e. essentially that quantity of coke deposited on the inert solids, is withdrawn by line 14 after passing through zone 13 where it is stripped with steam from line 32. Since any inert contact solids which are coke granules, the coke product is obtained as a relatively pure carbon material offering comparatively few problems with regards to the removal of contaminants.

To reduce the size of the coke particles, high velocity steam jets 11 and 12 effect attrition of the coke particles larger than about 250-300 microns to produce coke particles ranging from 75-250 microns. As will be appreciated by those skilled in the art, the necessary seed liquid for the conversion process is thus supplied. While a jet gas attritor has been shown as a preferred mode for supplying seed coke, a grinder or similar conventional means may be readily employed.

Shot catalyst is removed from the reactor through line 15 and conveyed by means of inclined conduit 17 and vertical riser 18 into heater vessel 2. Air, injected into the conveying passageway by means of line 16 and 19 serves to propel the shot catalyst, and additionally acts as a secondary source of oxygen for the burning operation. While a fluid bed heater is shown, a transfer-line burner, or a moving bed burner may be alternatively utilized.

Requisite air or other oxygen-containing gas for combusting the carbonaceous material deposited upon the shot catalyst particles is primarily supplied through line 20. Solids, thus heated by combustion to a temperature of about 1100° F., are withdrawn and returned to the conversion bed through line 22. Propellant gas such as steam or nitrogen is normally injected by line 23 to aid in circulating the relatively large sized particles back to the coking reactor. Gaseous products of combustion are removed from the heater by line 21. The unit can be maintained in heat balance by varying the circulation rate of the shot catalyst. For example, if more heat is required, the catalyst to oil ratio is increased. This increase in shot catalyst to the reactor increases the overall catalyst holdup, thereby deposing a greater amount of carbon on the catalyst and thus supplying the added fuel needed in the burner. However, it may be desirable under certain conditions of operation to supply an increased fuel to the combustion zone. In order to maintain the activity and selectivity level of the catalyst in the conversion zone 3, normally a portion of the circulating shot catalyst is subjected to treatment for the removal of its more contaminated surface layers. While the drawing illustrates the use of a jet attritor 25 operating in conjunction with heater 2, other means well known in the art, such as a ball mill type grinder, for accomplishing surface layer removal should be understood as falling within the scope of the present invention. Similarly, such a step may be employed at other points in the overall conversion process. As shown, catalyst particles pass from heater 2 through line 24 to attrition zone 25. A high velocity gas jet, preferably heated steam, is injected by line 27 and serves to wear away the outer layers of the catalytic solids thereby exposing fresh catalytic contacting surface. The openings of grid 26 are adjusted in size to permit the downflow of removed contaminants and catalytic solids less than 1000 microns in diameter, such particles passing out of the system through exit 29. Finely, entrained in expanded attrition gas, are withdrawn by line 28.

In order to maintain a relatively constant supply of catalytic solids, a fairly small amount of fresh shot catalyst may be added by line 31 into the stream of treated particles circulated back to heater 2 through line 30. Of course, unreacted catalysts may be introduced at other points in the process.

Thus, oil feed is subjected to a conversion treatment intermediate in nature between fluid coking and catalytic cracking.

The following summary illustrates the improved product distribution obtained by the present process when compared with conventional fluid coking operations. The feed in both cases is an 1100° F. + West Texas residuum, having a Conradson carbon content of 24.7%, and an A.P.I. gravity of 5.4.

<table>
<thead>
<tr>
<th>Products</th>
<th>Conventional Fluid Coking</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5, Wt. Percent</td>
<td>9.7</td>
<td>8.6</td>
</tr>
<tr>
<td>C7 Vol. Percent</td>
<td>9.1</td>
<td>9.1</td>
</tr>
<tr>
<td>C5-C9 F. Vol. Percent</td>
<td>16.5</td>
<td>20.2</td>
</tr>
<tr>
<td>400° F. to 500° F. Gas Oil, Vol. Percent</td>
<td>14.1</td>
<td>18.6</td>
</tr>
<tr>
<td>500° F. to 600° F. Gas Oil, Vol. Percent</td>
<td>29.2</td>
<td>37.6</td>
</tr>
<tr>
<td>Coke, Wt. Percent</td>
<td>27.3</td>
<td>24.4</td>
</tr>
<tr>
<td>Product Quality:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C5 + C6 F.</td>
<td>74.9</td>
<td>71.9</td>
</tr>
<tr>
<td>400° F. to 600° API</td>
<td>27.7</td>
<td>27.3</td>
</tr>
</tbody>
</table>

As shown above, the present process produces less gas and coke (low valued products) and more gasoline and gas oil of equal or better quality (high valued products) than conventional fluid coking.

The following table presents a compilation of pertinent ranges of conditions with regards to the process described:

<table>
<thead>
<tr>
<th>Reactor 1</th>
<th>Broad Range</th>
<th>Preferred Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °F.</td>
<td>900-1200</td>
<td>900-1050</td>
</tr>
<tr>
<td>Space Velocity, ft./hr.</td>
<td>25-50</td>
<td>35-50</td>
</tr>
<tr>
<td>Gas Vol. Percent</td>
<td>0.5-9</td>
<td>0.7-4</td>
</tr>
<tr>
<td>Space Velocity, ft./hr.</td>
<td>1-20</td>
<td>1-20</td>
</tr>
<tr>
<td>Catalyst/Oil Weight Ratio</td>
<td>3-6</td>
<td>3-6</td>
</tr>
</tbody>
</table>

While the above description has been limited to the use of a dense fluidized bed as the conversion zone, it should be understood that the application of large sized catalytic solids may be readily extended to dilute phase reaction systems such as a transfer line reactor. Additionally, it may be desirable to reactivate the surface of the catalytic particles and provide seed coke for the reaction bed in a single attrition system. Other modifications, apparent to those skilled in the art, may be applied to the system described without departing from the spirit of the present invention.

By using shot catalyst 3 as the primary means for directly supplying heat to a fluid coking process, numerous advantages are realized. Product quality and
distribution are improved while utilizing conventional equipment and coking procedures. The relatively large size of the heat-carrying catalytic particles provides for easy separation from inert bed solids. Additionally, contaminated surface layers may be readily removed while still maintaining a reasonably large catalytic surface area.

Having described the invention what is sought to be protected by Letters Patent is succinctly set forth in the following claims.

What is claimed is:

1. In a hydrocarbon conversion process wherein a residual hydrocarbon oil is introduced into a dense turbulent fluidized bed of inert particles averaging 40 to 400 microns in size and maintained in a conversion zone at a temperature in the range of 900° to 1200° F. for cracking said oil to vapors and carbonaceous material which deposits on said inert particles and solid cracking metal oxide-containing catalyst particles to be mentioned later on herein and wherein fluidizing gas passes upwardly through said conversion zone to maintain said inert particles in a dense turbulent fluidized condition and wherein said vapors pass upwardly and are withdrawn overhead, the improvement which comprises introducing solid cracking metal oxide-containing catalyst particles heated to a higher temperature than said inert solids into the lower portion of said dense turbulent fluidized bed for supplying heat and catalyst for cracking said oil, said solid cracking catalyst particles being larger than said inert particles and being in the range between about 1000 and 4000 microns in size, said solid cracking catalyst particles contacting said inert solids in the lower portion of said dense fluidized bed of inert particles in heat exchange relationship and settling downwardly therethrough to form a bed of solid cracking catalyst particles below said inert particles in the bottom of said conversion zone, passing said solid cracking catalyst particles from said bed of solid cracking catalytic particles to a regeneration zone to burn off carbonaceous deposits and to heat said solid cracking catalyst particles, and returning regenerated solid cracking catalyst particles to a regeneration zone to burn off carbonaceous deposits and to heat said solid cracking catalyst particles for converting said residual hydrocarbon oil introduced into said fluidized bed of inert solids.

2. A method according to claim 1 wherein said solid cracking catalyst particles are selected from the group consisting of activated clay, silica-alumina, silica-magnesia, and mixtures thereof.

3. A method according to claim 2 wherein the inert particles comprise coke particles and coke particles are withdrawn as product from the upper portion of said dense fluidized bed above the region of introduction of said larger solid cracking catalyst particles into said fluidized bed.

5. The process of claim 1, which further comprises passing steam upwardly through the bed of solid cracking catalyst particles in the lower portion of the coking zone, the steam being uniformly distributed for entry into the upper portions of said coking zone while stripping occluded hydrocarbons and admixed inert particles from said solid cracking catalyst particles.

6. An improved hydrocarbon oil conversion process for thermally and catalytically cracking residual hydrocarbon oil which comprises injecting a residual oil feed into a cracking and coking zone containing a fluidized bed of particulate inert solids averaging 40 to 400 microns in size and larger size solid cracking catalyst particles ranging from 1000 to 4000 microns in size maintained at a temperature in the range of about 900° to 1200° F. to convert the residual oil feed thermally and catalytically to gaseous products and coke which deposits on said bed inert and cracking catalyst particles, passing a fluidizing gas upwardly through said fluidized bed at a velocity sufficient to maintain a turbulent fluidized bed of inert and cracking catalyst particles while permitting said larger solid cracking catalyst particles to settle down into the lower portion of said cracking and coking zone, withdrawing and circulating a portion of said cracking catalyst particles to a regeneration zone to burn off coke deposits and heat the solid cracking catalyst particles to a temperature 100° to 400° F. hotter than said fluidized bed, and recycling the regenerated solid cracking catalyst particles thus heated to said cracking and coking zone to supply thermal energy for the thermal and catalytic conversion process.

7. The process of claim 6 which further comprises passing a portion of said withdrawn regenerated solid cracking catalyst particles to an attrition zone to remove contaminated outside layers from the surface of said solid cracking catalyst particles and to expose relatively fresh catalytic surfaces and circulating thus reactivated solid cracking catalyst particles back to said cracking and coking zone.

8. The process of claim 6 which further comprises passing a portion of said withdrawn cracking catalyst particles to an attrition zone wherein contaminated outside solid layers are removed and relatively fresh catalytic surfaces exposed, and circulating thus reactivated cracking catalyst particles back to said cracking zone.

References Cited in the file of this patent

UNITED STATES PATENTS

1,296,367 \[320,1919\] Cochran
2,459,915 \[419,1948\] Borcherding
2,506,307 \[519,1948\] Martin
2,627,499 \[535,1950\] Krebs
2,651,600 \[590,1953\] Tuff et al.
2,700,642 \[595,1955\] Mattix
2,723,223 \[605,1955\] Nicholson
2,736,687 \[605,1958\] Burnside
2,856,351 \[619,1958\] Welsy et al.