METHOD FOR PRODUCING LIGHT FUEL OIL

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Filed: Apr. 2, 1974

U.S. Cl. 208/77; 208/68; 208/70; 208/74; 208/76; 208/95

Int. Cl. C10G 37/06; C01b 33/28

Field of Search 208/77, 95

References Cited

UNITED STATES PATENTS

2,882,218 4/1959 Jewell 208/74
3,689,402 9/1972 Youngblood et al. 208/93
3,700,585 10/1972 Chen et al. 208/111
3,801,493 4/1974 Youngblood et al. 208/77
3,847,793 11/1974 Schwartz et al. 208/70

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ABSTRACT

A dual riser cracking operation of restricted hydrocarbon conversion is described wherein an intermediate fuel oil product of cracking higher boiling than the desired light fuel oil product is recovered and re-cracked in a first riser cracking zone in the presence of freshly regenerated catalyst and catalyst separated from the gasiform product of the first riser cracking zone is used in admixture with freshly regenerated catalyst in a second riser to crack higher boiling hydrocarbon charge in the presence of heavy recycle oil product under restricted conversion conditions to desired light fuel oil product. The riser may discharge into the lower portion of a dense fluid bed of catalyst.

10 Claims, 1 Drawing Figure
METHOD FOR PRODUCING LIGHT FUEL OIL

BACKGROUND OF THE INVENTION

The cracking of hydrocarbon charge stocks comprising gas oils and higher boiling residual material in the presence of finely divided catalyst particles has been a part of the petroleum refining procedure since the early forties. The cracking operations were for the purpose of producing gasoline along with lower and higher boiling products. It was also contemplated effecting the cracking operation in stages so that in one stage a more suitable feed could be produced for use in a latter hydrocarbon conversion stage. Such an operation including a restricted conversion operation is disclosed in the prior art of Jewell U.S. Pat. No. 2,882,218. In recent years crystalline aluminosilicate containing cracking catalysts have been developed and used for effecting cracking operations particularly for the production of gasoline as well as higher boiling products of the cracking operation. The present invention is concerned with the processing of crude oil distillation products in a novel combination of operating steps under conditions designed to particularly improve the recovery of desired light fuel oil product.

SUMMARY OF THE INVENTION

The present invention is concerned with an arrangement and combination of processing steps for producing a light fuel oil product. More particularly, the present invention is concerned with a limited hydrocarbon conversion operation and combination of processing steps particularly arranged to substantially maximize the production of light fuel oils boiling in the range of 320°F, up to about 700°F. from higher boiling gas oil type feed material separated from crude oil. In yet another aspect, the present invention is concerned with a dual riser hydrocarbon conversion operation maintained under particularly restricted hydrocarbon conversion conditions in the presence of cracking catalysts of selected activity. In the combination operation of this invention, a relatively light cycle oil product of the cracking operation generally higher boiling than the desired light fuel oil product and hereinafter referred to as a light intermediate cycle oil boiling from about 550°F, up to about 800°F, is selectively retracted in the presence of a freshly regenerated cracking catalyst under severely restricted or limited hydrocarbon conversion conditions not exceeding and preferably less than about 30 volume percent conversion. The freshly regenerated catalyst so used is thereafter stripped to remove entrained hydrocarbons and then cascaded to a second riser conversion zone along with added freshly regenerated cracking catalyst for conversion of fresh high boiling feed material such as a gas oil and higher boiling range materials under cracking conditions selected to restrict conversion thereof not to exceed about 40 percent and preferably the conversion is restricted to less than about 30 percent. Residual oils, atmospheric and vacuum reduced crude may be used with or in place of the gas oil feed.

In the combination operation comprising this invention, a light intermediate cycle oil (ICO) product of a restricted or limited hydrocarbon conversion or cracking operation and boiling in the range of about 550°F, up to about 800°F, is subjected to a restricted catalytic re cracking operation in a first riser reactor wherein the conversion is restricted to less than about 30 volume percent and preferably less than 20 volume percent. In this operation, the light intermediate cycle oil feed is admixed with hot freshly regenerated cracking catalyst of selected activity to form a suspension providing a catalyst/oil ratio in the range of about 2 to 10 and more usually less than about 8. The suspension is formed to provide a temperature less than about 950°F, and preferably the suspension temperature is within the range of 850°F to about 900°F. The thus formed suspension is provided a hydrocarbon residence time in a riser conversion zone within a range of 2 seconds up to about 2 minutes before encountering cyclonic separation. Thus, the riser reactor may discharge into the lower portion of a dense fluid bed of catalyst to provide increased residence time if desired. The longer residence time is particularly desired when the cracking catalyst includes ZSM-5 type of crystalline zeolite as an active component.

The catalyst is separated preferably by cyclonic means from the product of the intermediate cycle oil conversion operation and after stripping of the catalyst with gasiform material to remove entrained hydrocarbons, the stripped catalyst is cascaded to the inlet of a second riser conversion zone more fully discussed below.

In the second riser conversion zone, the high boiling feed plus any cycle oil boiling heavier than the intermediate cycle oil is combined with the previously used and cascaded catalyst combined with freshly regenerated catalyst to form a second suspension thereof at an elevated temperature providing a catalyst/oil ratio within the range of 4 to about 15. The oil-feed-catalyst mixture thus formed in the second riser is maintained at a temperature within the range of 850°F to about 950°F, during passage upwardly through the second riser conversion zone. A hydrocarbon residence time within the range of 2 to about 60 seconds in conjunction with the other operating parameters herein referred to restricts conversion of the heavy hydrocarbon feed to gasoline and lower boiling products not to exceed about 30 volume percent conversion and more usually not to exceed about 20 volume percent conversion. In the event, however, a more prolonged residence time for the gas oil conversion step is desired beyond that provided in the riser reactor, the second riser reactor may also discharge into a dense fluid bed of catalyst.

The catalyst compositions of desired and selected activity characteristics which may be employed in the combination operation of this invention may be formed from a number of different catalyst materials known in the art. That is, the catalyst may be an amorphous silica-alumina catalyst, a crystalline silica-alumina catalyst or preferably a crystalline zeolite catalyst of the "X" or "Y" type of faujasite. The faujasite and amorphous cracking components may be admixed with one another or either one or both of the larger pore materials may be mixed with a zeolite of a smaller pore size than the faujasite crystalline zeolite. In particular they may be mixed with either a ZSM-5 type of crystalline zeolite or a mordenite type of crystalline zeolite or a combination of each may be employed in relatively small amounts not exceeding and usually less than about 10 wt. percent.

Thus, it is contemplated employing catalyst compositions of restricted activity as measured by the fluid activity index (FAI) test within the range of from about
15 up to about 50 FAI. The FAI test is defined as the conversion obtained to a 356°F. at 90 percent ASTM gasoline product processing a light cost Texas gas oil at a temperature of 850°F., 2 c/o, 6 WHSV for 5 minutes on steam stream.

In the table below various catalyst compositions are shown which were tested and found to be suitable for use in the combination operation of the present invention.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>FAI Vol.% Conv.</th>
<th>Wt.% C on Cat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica + 10% Al₂O₃, Steamed at 1450°F.</td>
<td>22.7</td>
<td>0.16</td>
</tr>
<tr>
<td>Silica + 25% Al₂O₃, Steamed at 1400°F.</td>
<td>31.5</td>
<td>0.35</td>
</tr>
<tr>
<td>2% REY on Silica-clay-zirconia matrix</td>
<td>40.0</td>
<td>0.104</td>
</tr>
<tr>
<td>2% REY + 2% ZSM-5 on silica-clay-zirconia matrix</td>
<td>40.9</td>
<td>0.17</td>
</tr>
<tr>
<td>2% REY + 10% ZSM-5 on silica-clay-zirconia matrix</td>
<td>48.5</td>
<td>0.17</td>
</tr>
<tr>
<td>2% HZSM-5, matrix</td>
<td>17.7</td>
<td>0.06</td>
</tr>
<tr>
<td>2% REY + 2% H mordenite</td>
<td>41.4</td>
<td>0.094</td>
</tr>
<tr>
<td>2% REY + 10% H mordenite</td>
<td>38.6</td>
<td>0.095</td>
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</tbody>
</table>

**BRIEF DESCRIPTION OF THE DRAWING**

The drawing is a diagrammatic sketch in elevation of a dual riser conversion system with product fractionator and interconnecting conduit means for practicing the concepts of the invention.

**DISCUSSION OF SPECIFIC EMBODIMENTS**

Referring now to the drawing by way of example, there is shown a dual riser conversion system and related downstream steps for producing light cycle oil of desired pour point. In the arrangement of the drawing, an intermediate cycle oil product of the restricted conversion operation and boiling the range from about 550°F. up to about 800°F. is recovered from the product fractionation tower and passed by conduit 2 to riser conversion zone 4 of the dual riser conversion operation. Hot freshly regenerated catalyst is introduced to the lower portion of riser 4 by conduit 6 containing flow control valve 8. The freshly regenerated catalyst thus introduced is admixed with the recycled intermediate cyclo-oil product of cracking to form a relatively dilute suspension therewith at a temperature restricted to within the range of about 850°F. to about 900°F. The suspension at a catalyst to oil ratio within the range of 2 to 10 is caused to pass through the riser conversion zone to separation means provided adjacent, if not on, the discharge end thereof. In riser conversion zone 4, the hydrocarbon residence time is restricted to within the range of 2 to about 10 seconds but may be extended by discharging the riser into the lower portion of a dense fluid bed of catalyst. Conversion of the intermediate cycle oil to gasoline and lower boiling hydrocarbons is limited to less than 30 percent and preferably less than 20 percent.

The suspension passed through riser 4 discharges, when not passed into a dense fluid bed of catalyst, into cyclonic separation zone 10 wherein gasfio hydrocarbon material is separated from entrained catalyst particles. Separated hydrocarbons are passed overhead by conduit 12 to plenum chamber 14. Separated catalyist particles are passed from separator 10 by dipleg 16 to a bed of catalyst 18. Catalyst bed 18 is separated from an adjacent bed of catalyst discussed below by a vertical baffle member 20. The catalyst comprising bed 18 is stripped with stripping gas introduced by conduit 22 as the catalyst moves generally downward through a stripping zone 24 provided in the lower portion of vessel 26. Stripped catalyst is withdrawn from the lower portion of stripping zone 24 by conduit 28 provided with a flow control valve 30. The catalyst in conduit 28 is combined with freshly regenerated catalyst in conduit 32 provided with flow control valve 34. The catalyst stream thus formed is passed to the lower portion of a second riser conversion zone 36 to which fresh feed is introduced by conduit 38.

In the combination operation of this invention a heavy cycle oil product of the restricted conversion operation is recycled to the lower portion of riser 36 by conduit 40 for admixture with fresh gas oil feed.

In the lower portion of riser conversion zone 36, a suspension of catalyst particles in a relatively heavy hydrocarbon feed material, such as gas oils and heavy cycle oil, is formed having a temperature within the range of 850°F. to about 1100°F. and a catalyst to oil ratio within the range of 5 to about 20. A relatively inert gasfio material such as steam or light gaseous products of cracking may be combined with the heavy feeds passed to riser 36 to assist with vaporizing and mixing the oil charge with catalyst particles. In conversion zone 36, conversion of the high boiling feed material is restricted to below an upper limit of about 30 percent, it being preferred to restrict the level of conversion to be less than about 20 percent. A space velocity within the range of 50 to about 200 v/v/hr. may be employed in cooperation with a selected temperature and catalyst to oil ratio so as to limit conversion of the oil charge as herein provided. The suspension is passed upwardly through riser 36 and into cyclonic separating means 42 when a dense fluid bed of catalyst is not employed, provided on the discharge end of riser 36. Gasfio hydrocarbon material separated from the catalyst is passed from separator 42 by conduit 44 to plenum 14. Separated catalyst particles are passed by dipleg 46 to a bed of catalyst 48 confined within a separate stripping section 50 in the lower portion of vessel 26. Catalyst bed 48 is separated from catalyst bed 18 by vertical baffle 20. Stripping gas is introduced to a lower portion of bed 48 by conduit 52 for flow upwardly through the descending bed of catalyst.

Stripped products of hydrocarbon conversion and stripping gas removed from the upper surfaces of catalyst beds 18 and 48 pass upwardly through the vessel 26 to cyclone separation means 54 wherein stripped hydrocarbons and stripping gases are separated from any entrained catalyst particles. Separated catalyst is returned by dipleg 56 to a bed of catalyst shown to be bed 18 and vapoous material is passed by conduit 58 to plenum 14.

The hydrocarbons separated from catalyst and passed to plenum chamber 14 are removed therefrom by conduit 60 communicating with a fractionation tower 62. In fractionation zone 62 a separation is made to recover materials lower boiling than desired light fuel oil product from an upper portion thereof by conduit 64. The material withdrawn by conduit 64 and comprising gasoline and lower boiling hydrocarbons
may be separated in equipment not shown into desired components for further treatment as desired. A light fuel oil product boiling in the range of 320°F to about 750°F and preferably in the range of 400°F to about 675°F is withdrawn by conduit 64 communicating with zone 68 wherein the light fuel oil pour point is improved by contact with a ZSM-5 type of crystalline zeolite conversion catalyst. In zone 68, the ZSM-5 catalyst retained as a fluid bed of catalyst at a temperature in the range of 500°F to 850°F and a pressure in the range of 50 to 100 psig reduces the pour point of the light fuel oil charge depending upon the severity of the operation employed to within a range of -30°F to about +15°F. Light fuel oil of desired reduced pour point is withdrawn by conduit 76. Recently issued U.S. Pat. No. 3,702,886 describing and claiming ZSM-5 type crystalline aluminosilicate is incorporated herein by reference.

A relatively sloppy intermediate cycle oil fraction boiling in the range of from about 550°F to about 800°F is withdrawn from the fractionator 62 by conduit 72 communicating with conduit 2 and is recycled as the feed to the first riser conversion zone as discussed above.

A heavy cycle oil product fraction boiling in the range of 600°F to about 950°F is withdrawn from fractionator 62 by conduit 74. All or a portion of this heavy cycle oil may be recycled by conduit 40 for admixture with the fractionated product.

A clarified slurry oil fraction is withdrawn from a bottom portion of lower 62 by conduit 76.

In the arrangement of the drawing, the lower portion of vessel 26 is shown separated by baffle 20 into two separate stripping zones 24 and 50. Stripped catalyst is withdrawn from the lower portion of zone 50 containing catalyst bed 48 by conduit 78 provided with flow control valve 80 for passage to a catalyst regeneration zone not shown wherein deposited carbonaceous material more often referred to as coke is removed from the catalyst by burning thereby heating the catalyst to a desired elevated temperature within the range of 1,200°F to 1,400°F. The catalyst thus heated is then available for use and return to the riser conversion zones by conduits 6 and 32 as shown. In the catalyst system of this invention it is contemplated discharging each riser or either one into the lower portion of a catalyst bed for flow upward therethrough as herein before provided, or employing a single bed of catalyst collected from each riser conversion zone in a stripping zone from which catalyst is cascaded to both the regeneration zone as well as the second riser conversion zone. In this latter arrangement, a desired relatively high catalyst to oil ratio may be provided for promoting a restricted conversion of the oil charged to the riser.

It is also contemplated using the dual riser conversion operation herein defined so that the fresh gas oil feed rather than the intermediate light fuel oil is passed to riser 1 for contact with freshly regenerated catalyst, the intermediate cycle oil product rather than fresh feed is passed to riser 2 for contact with a catalyst mixture which is primarily freshly regenerated catalyst. It is contemplated employing a single bed catalyst stripping zone with provisions for recycling catalyst to either riser for adjustment of catalyst to oil ratio and temperature best suited for performing the restricted conversion operation of this invention. In any of the arrangements employed, it is important to re-crack the intermediate cycle oil separately under conversion conditions preferably limited to less than 20 percent conversion. On the other hand, the heavy cycle oil may be processed with the fresh feed passed to the combination operation whether it be a gas oil or higher boiling residual material as herein contemplated.

In addition, feed preheat may be practiced on feed passed to either riser up to the maximum allowable before substantial thermal cracking of the feed occurs. Having thus generally described the method and concepts of the present invention and discussed specific embodiments going to the very essence thereof, it is to be understood that no undue restrictions are to be imposed by reason thereof except as defined by the following claims.

We claim:

1. A method for producing light cycle oil from higher boiling hydrocarbon feed materials which comprises, passing a relatively high boiling hydrocarbon feed material with a cracking catalyst of limited activity through a first conversion zone maintained under conditions to limit conversion of the hydrocarbon feed to gasoline and lower boiling products, recovering a hydrocarbon phase from said first conversion zone and separating in a fractionation zone said hydrocarbon phase into a desired light fuel oil product, an intermediate cycle oil product and a higher boiling cycle oil product, passing said higher boiling cycle oil product to said first conversion zone, passing said intermediate cycle oil product to a second conversion zone for contact with a cracking catalyst of limited activity under limited conversion conditions particularly selected to produce light fuel oil product, and recovering said light fuel oil product in said fractionation zone, passing catalyst separated from said second conversion zone to said first conversion zone, and reducing the pour point of said light fuel oil product recovered from said conversion operations by contact with a ZSM-5 type of crystalline zeolite.

2. The method of claim 1 wherein the hydrocarbon conversion steps are restricted not to exceed about 30 volume percent in each zone.

3. The method of claim 1 wherein the activity of the catalyst employed in the conversion steps is restricted to within the range of 15 to 50 FAI.

4. The method of claim 1 wherein hot regenerated catalyst is passed to each of said conversion zones.

5. The method of claim 1 wherein each of said conversion zones comprises at least a riser conversion zone and the hydrocarbon residence time within the first conversion zone is restricted to within the range of 2 to 60 seconds.

6. The method of claim 1 wherein the catalyst of selected and limited activity is made from catalyst components selected from the group comprising amorphous silica alumina, crystalline zeolites of the faujasite type and mixtures thereof in combination with one or more of a ZSM-5 type of crystalline aluminosilicate and a mordenite type of crystalline zeolite.

7. The method of claim 1 wherein the intermediate cycle oil product of cracking used as feed in the second conversion zone boils in the range of about 550°F up to about 800°F.

8. The method of claim 1 wherein the light fuel oil product of the hydrocarbon conversion zones boils in
the range of 320°F to about 700°F and contact thereof with the ZSM-5 type catalyst reduces its pour point to within the range of −30°F to about 15°F.

9. The method of claim 1 wherein each of said conversion zones comprises a riser conversion zone discharging into a fluid bed of catalyst before separation of a hydrocarbon phase from a catalyst phase is effected.

10. A method for producing light fuel oil product of desired pour point which comprises,

separating an intermediate cycle oil product of cracking higher boiling than desired fuel oil product obtained as hereinafter defined,

re-cracking said separated intermediate cycle oil product in a first riser cracking operation in the presence of freshly regenerated catalyst of restricted activity under conditions selected to restrict conversion thereof to less than 30 vol. percent,

separating the product of said re-cracking operation to recover a hydrocarbon phase from a first catal-

yst phase and passing said hydrocarbon phase to a product fractionation zone,

passing catalyst from said first catalyst phase to a second riser conversion zone, passing freshly regenerated catalyst along with fresh gas oil feed and heavy cycle oil product of cracking to said second riser cracking zone,

effecting cracking of the hydrocarbon feed passed to said second riser cracking operation under conversion condition restricted to less than about 40 vol. percent,

separating the product of said second riser cracking operation into a hydrocarbon phase and a second catalyst phase, passing the hydrocarbon phase to said product fractionation zone, and reducing the pour point of a light cycle oil separated from the product of cracking operation by contacting a ZSM-5 type of crystalline zeolite under selected conversion conditions.

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