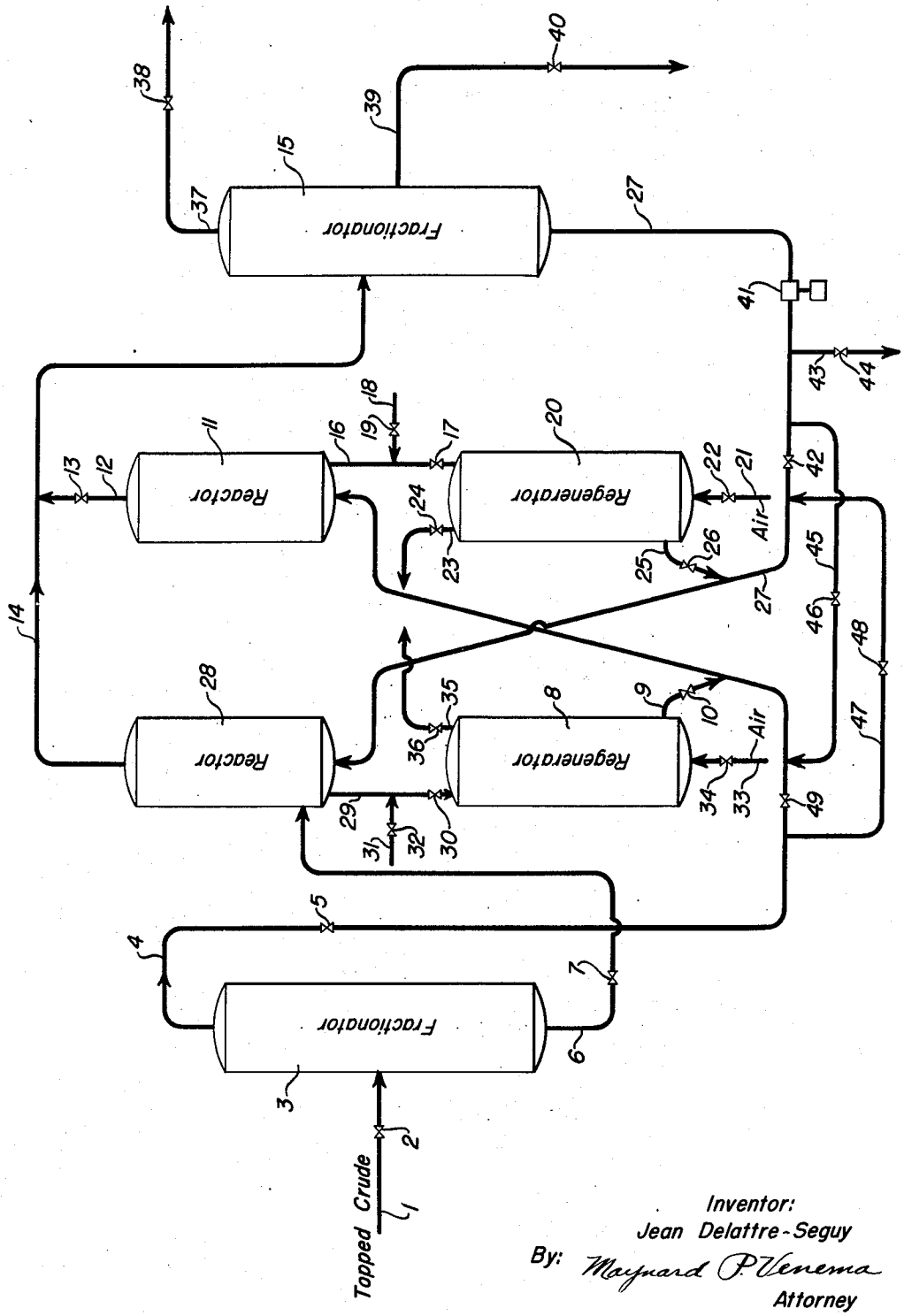
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CATALYTIC CRACKING OF HYDROCARBONS

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CATALYTIC CRACKING OF HYDROCARBONS

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This invention relates to the catalytic cracking of hydrocarbons. It is more particularly concerned with the conversion of high boiling hydrocarbons such as topped or reduced crudes to high octane number gasolines by a two step process employing fluidized catalyst.

In order to obtain a greater amount of gasoline from a given amount of crude oil, it is necessary to crack the heavier or residual portions of the crude. To utilize these high boiling fractions as charging stocks for catalytic cracking processes, it has been necessary in the past to remove the coke-forming constituents, such as asphaltenes and the like, by relatively expensive methods such as propane deasphalting, vacuum distillation, and steam distillation. Even then the resultant material often was found to be an undesirable charge stock, particularly in fluid catalyst systems, because it was difficult to vaporize and process, and because it cracked to excessive amounts of low grade products such as coke or gas when contacted with active, freshly regenerated catalyst.

I have invented an improved economical process for cracking residual oils to good yields of gasoline without excessive production of gas or coke, and with our prior treatment or removal of asphaltenes and the like from the oil.

In one embodiment my invention relates to a process for the conversion of hydrocarbons which comprises separating a hydrocarbon oil containing intermediate and residual fractions of petroleum into a gas oil fraction and a residual fraction, subjecting the gas oil fraction to the action of hot, freshly regenerated cracking catalyst at cracking conditions in a first cracking step, separating the catalyst from the hydrocarbons in said step, passing the catalyst so separated to a first regeneration zone wherein the carbonaceous deposit is burned from the catalyst, separately withdrawing the catalyst from said regeneration zone and contacting it with a heavy reflux condensate, produced as hereinafter described, contacting the resultant mixture with said residual fraction in a second cracking step at cracking conditions, withdrawing the catalyst from contact with the hydrocarbons and discharging it into a second regeneration zone wherein the carbonaceous deposit is burned therefrom, supplying the hot regenerated catalyst to said first cracking step, combining the hydrocarbon effluents from said cracking steps, fractionating the same to obtain a light and a heavy reflux condensate boiling above the gasoline range, and recycling at least a portion of the heavy reflux condensate to the second cracking step.

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In a more specific embodiment my invention relates to a process such as that described above further characterized in that relatively severe cracking conditions are maintained in the first cracking step and less severe cracking conditions are maintained in the second cracking step.

Briefly stated, my invention, as applied to a cracking process employing fluid catalyst, comprises distilling a hydrocarbon oil such as topped crude to separate a gas oil and a liquid residue. The gas oil, being a rather refractory stock, is used to transfer hot, freshly regenerated cracking catalyst to a reactor wherein it is cracked selectively at temperatures in the range of from about 940° F. to about 1100° F. and at a space velocity and catalyst to oil ratio sufficient to give an appreciable conversion to lower boiling hydrocarbons. The catalyst in this zone is separated from the hydrocarbons and is passed into a first regeneration zone wherein the carbonaceous deposits are removed from the catalyst by oxidation. The regenerated catalyst is separately withdrawn and is contacted with a relatively refractory stream of heavy reflux condensate, produced as hereinafter described, after which the catalyst in admixture with the more refractory oil is contacted with the liquid residue in a second cracking zone, at cracking conditions less severe than those maintained in the first cracking zone. The temperature in this second cracking step usually will lie within the range of from about 850 to about 940° F. The catalyst from this zone is separated from the hydrocarbons, is passed to a regenerator wherein the carbonaceous deposits are burned therefrom, and the regenerated catalyst is returned to the first cracking zone. The hydrocarbon effluents from the cracking zones are combined, are fractionated to obtain a light and a heavy reflux condensate boiling above the gasoline range, and at least a portion of the heavy reflux condensate is recycled to the second cracking step.

One of the advantages of this process is the separation of a hydrocarbon oil containing intermediate and residual fractions of petroleum into a gas oil fraction and a residual fraction and the conversion of these fractions into motor fuel constituents by processing each fraction under conditions of temperature and catalyst activity most favorable for that particular stock. Since the virgin gas oil fraction is relatively refractory, it should be cracked at more severe conditions, i. e., at a fairly high temperature and in the presence of a relatively active catalyst such as freshly regenerated catalyst. These conditions are much too drastic for the liquid residue; for

it has been found that at these conditions the residue is converted chiefly into gas and coke. However, at temperatures within the range of from about 850 to 940° F. and in the presence of a partially carbonized catalyst and a somewhat lighter oil, the residue can be more selectively converted into motor fuel constituents. Contacting the hot, freshly regenerated catalyst from the first regeneration zone with heavy reflux condensate serves to lower the temperature of the catalyst and to deposit some carbonaceous material thereon, thereby lowering its activity and preparing it for subsequent contact with the liquid residue. The initial activity of the catalyst is not dissipated by this method of operation because said activity is utilized in cracking a portion of the heavy reflux condensate.

Because the liquid residue has greater coke-forming tendencies than the virgin gas oil, the catalyst passing from the second cracking zone to the second regeneration zone usually contains a greater amount of carbonaceous deposit than the catalyst passing from the first cracking zone to the first regeneration zone. As a consequence, the temperature in the second regeneration zone is higher than that in the first. This is advantageous because the hotter catalyst from the second regeneration zone is used in the high temperature cracking step and the cooler catalyst from the first regeneration zone is used in the lower temperature cracking step. This is one of the chief reasons for using two regeneration zones instead of a single, common regenerator.

Further advantages of my process will be apparent from the following description of the accompanying drawing which illustrates in conventional side elevation one form of apparatus in which the present invention may be accomplished. For purposes of simplification, certain auxiliary equipment such as condensers, reflux accumulators, and the like have been omitted from the drawing, but it is to be understood that such equipment is to be used wherever engineering skill dictates.

Referring now to the drawing, substantially gasoline-free crude oil is passed through line 1 containing valve 2 into fractionator 3 wherein the vaporous gas oil fraction is removed overhead through line 4 containing valves 5 and 49 and a liquid residue is removed as a bottoms product through line 6 containing valve 7.

Hot regenerated catalyst in a fluidized form such as a powder or microspheres, present in regenerator 8, is passed through line 9 containing valve 10 into line 4 wherein it is picked up by the vaporous gas oil fraction from fractionator 3, and the resultant mixture is passed into cracking zone 11. The temperature within this zone is maintained at from about 940° F. to about 1100° F. and the reaction time is regulated to give substantial conversion, i.e., from about 40 to about 85% conversion based on the gas oil charged thereto. In this zone some carbonaceous material is deposited on the catalyst thereby lowering its activity.

Any suitable metal oxide cracking catalyst such as silica-alumina, silica-zirconia, silica-alumina-zirconia, silica-magnesia, silica-alumina-magnesia, alumina-boria, and the like, may be employed. These catalysts may be prepared in any suitable manner including separate, successive, and coprecipitation methods. In some cases, naturally occurring materials such as montmorillonite or acid treated montmorillonite may be employed.

A dense phase bed of solid catalyst particles is maintained in reactor 11 and is kept in a fluid-like state of relatively high density by the hydrocarbons passing upwardly through the bed at a velocity which partially counteracts the force of gravity on the solid particles and brings about their hindered settling within the dense phase bed. Above the dense phase bed in the upper portion of the reaction chamber a relatively light phase region having a reduced catalyst density is maintained, wherein the catalyst is substantially separated from the hydrocarbons by means of a separator, such as a cyclone separator, not shown on the drawing. The cracked products are discharged from the upper end of reactor 11 through line 12 containing valve 13 and are directed through line 14 into fractionator 15.

The carbonized catalyst from reactor 11 is withdrawn through line 16 containing valve 17 and flows downwardly and countercurrently to an upwardly flowing stream of stripping medium, such as steam, which enters line 16 through line 18 containing valve 19. The stripped catalyst is passed into regenerating zone 20 wherein carbonaceous deposits on the catalyst are removed by oxidation. This is accomplished by passing an oxidizing gas, such as air, through line 21 containing valve 22 into the bottom of regenerator 20. The air passes upwardly through the catalyst and leaves the regenerator via line 23 containing valve 24. Entrained catalyst particles are removed from the air stream by means of a cyclone separator or the like, and are returned to the dense phase maintained in regenerator 20.

Hot regenerated catalyst from regenerator 20 is passed through line 25 containing valve 26 and is passed into line 27 wherein it is commingled with a recycle stream of heavy reflux condensate. The mixture of catalyst and condensate passes through line 27 into the bottom of reactor 28 wherein is maintained a light and a dense phase of solid catalyst particles in a manner similar to that described in connection with reactor 11. Liquid residue flowing through line 6 is injected into the lower portion of the dense phase in reactor 28. The temperature maintained in this reactor usually lies within the range of from about 850° F. to about 940° F. The conversion products, from which entrained catalyst has been separated, are discharged from reactor 28 through line 14 and are directed into fractionator 15.

The catalyst in reaction zone 28 is withdrawn through line 29 containing valve 30 and is directed downwardly and countercurrently to the upwardly flowing stripping medium which enters line 29 through line 31 containing valve 32. The catalyst flowing through line 29 passes into regenerator 8. The oxidizing gas employed for burning the combustibles on the contaminated catalyst is supplied to regenerator 8 through line 33 containing valve 34. The flue gases are discharged from the upper end of the regenerator by means of line 35 containing valve 36 after being passed through suitable catalyst separation means.

In fractionator 15 the hydrocarbon effluents from the reactors are separated into several fractions. Gasoline and gaseous hydrocarbons are removed overhead from the fractionator through line 37 containing valve 38. A light reflux condensate is removed as a side cut through line 39 containing valve 40. This light reflux condensate is rather refractory and, hence, it usually is not

recycled to the cracking step. Because of its relatively high aromatic content, it is useful as a solvent, in the production of naphthalene, and the like. Heavy reflux condensate is withdrawn from the bottom of fractionator 15 through line 27, pump 41, and valve 42. A portion of this stream may be withdrawn to storage or other conversion processes through line 43 containing valve 44. In order to balance out the process, it may be desirable to pass a portion of the heavy reflux condensate to reactor 11 or a portion of the virgin gas oil to reactor 28. This may be done by utilizing line 45 containing valve 46 or line 47 containing valve 48, respectively.

In general, the pressures maintained on the reactors and regenerators will lie below 100 p. s. i. and preferably below 50 p. s. i.

Although my process has been described in connection with a fluidized catalyst system, it is to be understood that it is also applicable to systems in which the catalyst is transported as a compact moving bed.

I claim as my invention:

1. A process for the conversion of hydrocarbons which comprises separating a hydrocarbon oil containing intermediate and residual fractions of petroleum into a gas oil fraction and a residual fraction, subjecting the gas oil fraction to the action of hot, freshly regenerated cracking catalyst at cracking conditions in a first cracking zone, separating the catalyst from the hydrocarbons, passing separated catalyst from said cracking zone to a first regeneration zone and therein burning the major portion, at least, of the carbonaceous matter therefrom, withdrawing regenerated catalyst from said first regeneration zone and contacting the same with said residual fraction in a second cracking zone under conditions to convert a substantial portion of said residual fraction into gasoline, removing contaminated catalyst from said second cracking zone and introducing the same to a second regeneration zone, separately removing the cracked vapors from said second cracking zone and supplying the same directly and without prior passage through said first cracking zone to a fractionating zone, separating said gasoline from the cracked vapors in the fractionating zone, regenerating said contaminated catalyst in the second regeneration zone at higher temperature than the catalyst in said first regeneration zone, and supplying hot regenerated catalyst from said second regeneration zone to said first cracking zone.

2. The process of claim 1 further characterized in that said first cracking zone is maintained at a temperature of from about 940° F. to about 1100° F. and the second cracking zone at a temperature of from about 850° F. to about 940° F.

3. A process for the conversion of hydrocarbons which comprises separating a hydrocarbon oil containing intermediate and residual fractions of petroleum into a gas oil fraction and a residual fraction, subjecting the gas oil fraction to the action of hot, freshly regenerated cracking catalyst at cracking conditions in a first cracking zone, separating the catalyst from the hydrocarbons, passing separated catalyst from said cracking zone to a first regeneration zone and therein burning the major portion, at least, of the carbonaceous matter therefrom, transferring hot regenerated catalyst from said first regeneration zone to a second cracking zone, commingling reflux condensate, formed as hereinafter set forth, with the regenerated catalyst in transit from the regeneration zone to the second cracking zone to reduce the temperature and activity of the regenerated catalyst, introducing said residual fraction to the second cracking zone and therein contacting the same with the regenerated catalyst of reduced temperature and activity under conditions to convert a substantial portion of said residual fraction into gasoline, removing contaminated catalyst from said second cracking zone and discharging the same into a second regeneration zone, separately removing the cracked vapors from said second cracking zone and supplying the same directly and without prior passage through said first cracking zone to a fractionating zone, separating said gasoline from the cracked vapors in the fractionating zone, regenerating said contaminated catalyst in the second regeneration zone at higher temperature than the catalyst in said first regeneration zone, supplying hot regenerated catalyst from said second regeneration zone to said first cracking zone, supplying the vapors from said first cracking zone to said fractionating zone and withdrawing from the last-named zone a reflux condensate boiling above the gasoline range, and commingling at least a portion of said reflux condensate with the hot regenerated catalyst in transit from said first regeneration zone to said second cracking zone as aforesaid.

4. The process of claim 3 further characterized in that said first cracking zone is maintained at a temperature of from about 940° F. to about 1100° F. and the second cracking zone at a temperature of from about 850° F. to about 940° F.

5. The process of claim 3 further characterized in that the vapors from said cracking zones are fractionated in said fractionating zone to separate light and heavy reflux condensates therefrom and at least a portion of the heavy reflux condensate commingled with the hot regenerated catalyst in transit from said first regeneration zone to said second cracking zone.

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