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CONVERSION OF HYDROCARBONS

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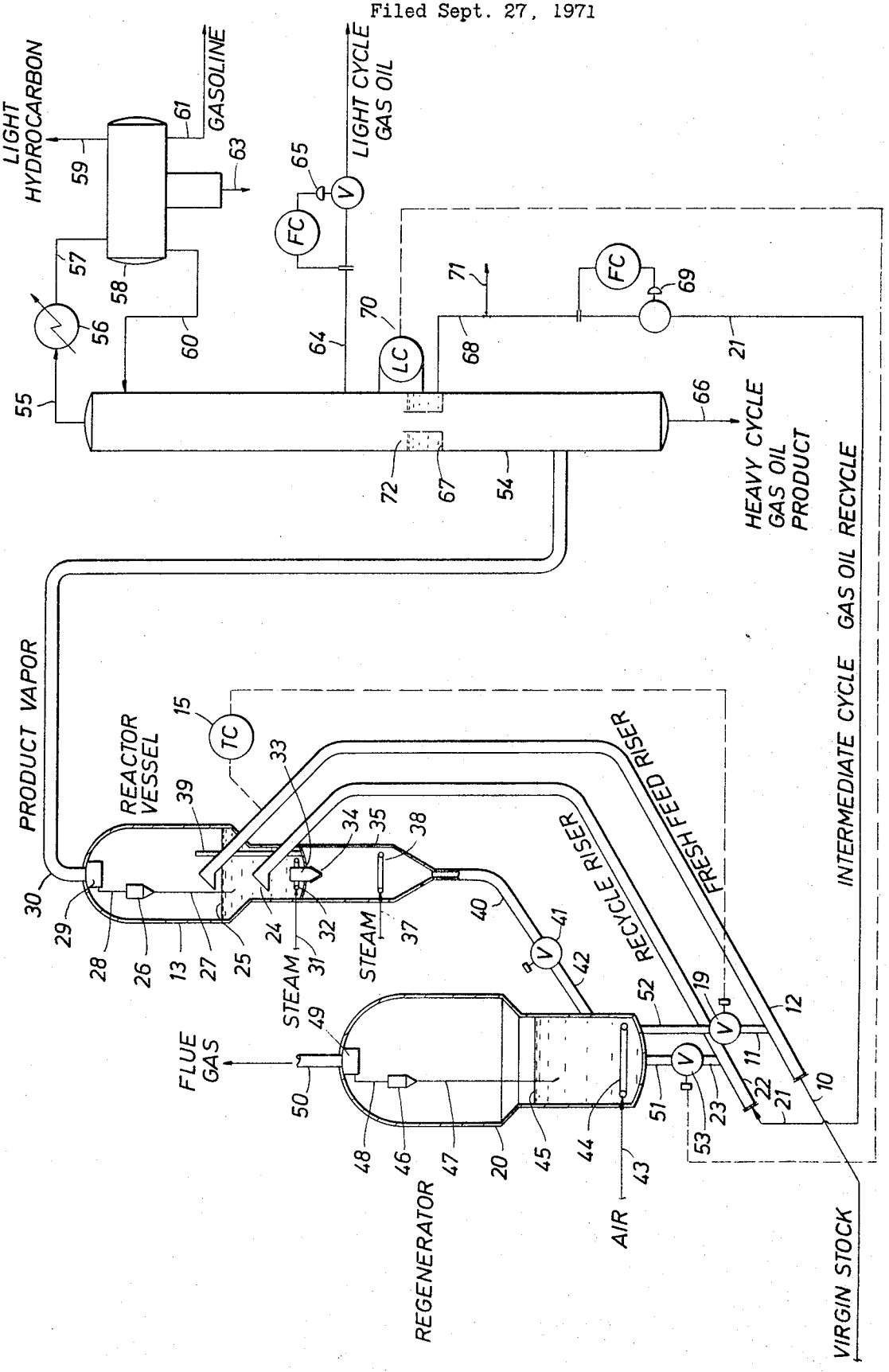

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CONVERSION OF HYDROCARBONS

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ABSTRACT OF THE DISCLOSURE

A fluidized catalytic cracking process for the conversion of hydrocarbons comprising a reaction zone, a regeneration zone and a product fractionation zone. A selected product distribution, such as between gasoline and light cycle gas-oil, is maintained by recovering light cycle gas-oil at a selected rate from the product fractionation zone, and controlling hydrocarbon conversion in the reaction zone to maintain a set rate for a heavy cycle gas-oil recycle stream. The gasoline product is recovered from the product fractionation zone at the rate it is produced. Process control means for operating the process in the above manner are disclosed.

BACKGROUND OF THE INVENTION

This invention relates to fluidized catalytic cracking. More particularly, it relates to a method for controlling a fluidized catalytic cracking process to obtain a desired product distribution.

In a fluidized catalytic cracking process, hydrocarbon oil is contacted with catalyst in a reaction zone under conditions such that hydrocarbon is converted into desired products with a concomitant deposition of coke upon the catalyst. Catalyst removed from the reaction zone may be contacted in a stripping zone with a stripping medium to removed occluded hydrocarbon oils therefrom. The stripping medium and removed hydrocarbon may be passed from the stripping zone into the reaction zone. From the stripping zone, stripped catalyst may be passed into a regeneration zone wherein the stripped catalyst is regenerated by burning coke therefrom employing an oxygen containing gas such as air. From the regeneration zone, hot regenerated catalyst may be withdrawn and contacted with additional hydrocarbon in the reaction zone. Hydrocarbon vapor from the reaction zone may be passed into a fractionation zone wherein the vapor is separated into component fractions according to boiling range. A gasoline and lighter component fraction may be recovered overhead from the fractionation zone, and a heavy cycle gas-oil fraction may be recovered as a bottom product from the fractionation zone. A light cycle gas-oil fraction, suitable for use as a heating oil, may be recovered as one liquid side draw from the fractionation zone. An intermediate cycle gas-oil fraction may be collected in an accumulation section within the fractionation zone from which a second cycle gas-oil stream may be withdrawn. All or a portion of the intermediate cycle gas-oil stream may be recycled from the fractionation zone to the reaction zone for further conversion into desirable products.

The yield of desirable products from such a fluidized catalytic cracking process may be controlled within a certain range by selecting the hydrocarbon conversion conditions within the reaction zone and by selecting the intermediate cycle gas-oil recycle rate from the fractionation zone to the reaction zone. For instance, the rate of product of light cycle gas-oil may be increased at the expense of other products during the months when the commercial demand for heating oil is high, and may be decreased with a concomitant increase in gasoline production during the months when gasoline demand is high.

Hydrocarbon oils charged to the reaction zone are heated to an elevated temperature of from about 450° F. to about 750° F. Preferably, the preheat temperature of the hydrocarbon does not exceed the temperature at which substantial thermal cracking begins to occur. Such hydrocarbon preheat temperatures are generally below the desired reaction temperatures. The additional heat required to raise the temperature of the hydrocarbon in the reaction zone to the desired reaction temperature is provided by the hot, regenerated catalyst. In the regeneration zone, when coke is burned from the stripped catalyst, the temperature of the regenerated catalyst increases to a temperature in the range of from about 1100° F. to about 1250° F. A desired regenerated catalyst temperature may be obtained by controlling the amount of heat which is removed from the regeneration zone.

A preferred reaction temperature for the conversion of hydrocarbons is from about 880° F. to about 985° F. The hydrocarbon oil is preheated to a temperature such that regenerated catalyst may be added in a catalyst to oil weight ratio of from about 3 to about 15 to increase the hydrocarbon temperature to the selected reaction zone temperature while maintaining an acceptable regeneration zone temperature.

A known method for operating a fluid catalytic cracking process to obtain desired products in a selected ratio comprises preheating the hydrocarbon feed to a selected temperature; controlling the addition of regenerated catalyts to the hydrocarbon to maintain a selected reaction zone temperature; and recycling intermediate cycle gas-oil at a selected rate. The gasoline and lighter product fraction is recovered from the fractionation zone as it is produced. The heavy cycle gas-oil fraction is also recovered from the fractionation zone as it is produced. The light cycle gas-oil is recovered from the fractionation zone at a rate so as to maintain a constant level of intermediate cycle gas-oil in the accumulation section of the fractionation zone. The intermediate cycle gas-oil recycle rate and the reaction zone temperature may be varied to obtain the desired product distribution. For instance, increasing the reaction zone temperature increases the rate of production of light components in the product, and increasing the intermediate cycle gas-oil recycle rate decreases the light cycle gas-oil yield since a portion of the light cycle gas-oil must be allowed to collect upon the intermediate cycle gas-oil trap tray to maintain the liquid level thereon. By properly selecting the intermediate cycle gas-oil recycle rate and the reaction zone temperature, a wide range of product distribution between the light components, the gasoline component, and the light cycle gas-oil fraction may be obtained. One disadvantage to this method of controlling the operation of a fluid catalytic cracking process is that both the reaction zone temperature and the intermediate cycle gas-oil recycle rate must be adjusted simultaneously in order to obtain the desired product distribution.

SUMMARY OF THE INVENTION

Now, in accordance with the method of the present invention, I have discovered an improved method for controlling the operation of a fluidized catalytic cracking process to obtain a desired product distribution. More particularly, the method of the present invention comprises withdrawing light cycle gas-oil from the fractionation zone at a selected rate; recycling intermediate gas-oil from the fractionation zone to the reaction zone at a set rate; and maintaining an essentially constant gas-oil liquid level in the accumulation section of the fractionation zone by adjusting the ratio of regenerated catalyst to hydrocarbon in the reaction zone.

The advantage of this method for controlling the operation of a fluidized catalytic cracking process is that

light cycle gas-oil may be produced at a rate commensurate with the market demand for such product and the product distribution between gasoline and lighter components may be adjusted through a wide range by varying the intermediate cycle gas-oil recycle rate.

BRIEF DESCRIPTION OF THE DRAWINGS

The attached drawing is a schematic diagram of a fluid catalytic cracking process embodying the improved control method of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Fluid catalytic cracking processes such as hereinabove described are well known to the prior art. Virgin hydrocarbon charge stock to such fluid catalytic cracking processes such as, for example, distillate fractions from crude petroleum are also well known in the prior art. A wide variety of catalysts such as synthetic silica alumina, synthetic silica magnesia, silica alumina zeolite, natural clays, acid treated natural clays, etc. are available for utilization within a fluid catalytic cracking process. A further description of such items is not required herein.

In the development of fluid catalytic cracking it has been found that an improved yield of gasoline and light cycle gas-oil is obtained by employing a relatively short contact period of good contact between hydrocarbon and catalysts in the reaction zone as compared to a longer period of poor contact. Improved contact between hydrocarbon and catalyst may be obtained employing a reaction zone configuration comprising a reaction vessel, located adjacent to and above a regeneration zone, and a riser conduit. When this configuration is employed, hydrocarbon enters the lower end of the riser and regenerated catalyst is admitted to the riser from the regeneration zone. Catalyst and hydrocarbon flow upward through the riser under reaction conditions such that a substantial portion of the hydrocarbon conversion occurs in the riser. The hydrocarbon-catalyst mixture discharges from the riser into the reaction vessel. In the reaction vessel an inventory of catalyst is maintained in a fluidized condition by the passage therethrough of the discharged hydrocarbon vapors, and other vapors such as, for example, primary stripping steam. The location of the riser discharge into the reactor vessel is determined such that the discharged hydrocarbon vapors are in contact with the catalyst inventory of the reaction vessel for a time sufficient to obtain the desired additional hydrocarbon conversion in the reaction vessel. The desired catalyst inventory is maintained in the reaction vessel by removing catalysts into a stripping zone. In the stripping zone, occluded hydrocarbons are separated from the catalyst employing a stripping vapor. The stripping vapor and separated hydrocarbons are passed into the reaction vessel and the stripped catalyst is passed into the regeneration zone. The carbonaceous deposits known as coke are burned from the stripped catalysts employing an oxygen containing gas such as air in the regeneration zone. Regenerated catalyst is passed from the regeneration zone into the riser for contact with additional hydrocarbons.

Hydrocarbon vapor is recovered from the reactor vessel and passed into a fractionation zone wherein the vapor may be separated into a gasoline and lighter fraction, a light cycle gas-oil fraction as liquid side draw from the fractionation zone, and a heavy cycle gas-oil fraction as a bottom product from the fractionation zone. The fractionation zone is equipped with means such as a trap tray for collecting a volume of intermediate cycle gas-oil in an accumulating section of the fractionation zone. An intermediate cycle gas-oil recycle stream is withdrawn from said fractionation zone at a selected rate and passed to the reaction zone for additional conversion in the presence of regenerated catalyst.

In applying the method of the present invention to such a fluidized catalytic cracking process, the fractionation zone may be provided with a level indicating means to determine the amount of intermediate cycle gas-oil accumulated within the accumulation section. The gasoline and lighter fraction is recovered from the fractionation zone as it is produced, the light cycle gas-oil is recovered from the fractionation zone at a selected rate and the intermediate cycle gas-oil recycle stream from the fractionation zone to the reaction zone is established at a set rate. Catalyst from the regeneration zone is admitted into the reaction zone at a catalyst to oil ratio adjusted to maintain a desired intermediate cycle gas-oil liquid level within the accumulation section. The product distribution between gasoline and lighter components is adjusted into the desired range by properly selecting the heavy cycle gas-oil recycle rate. The heavy cycle gas-oil fraction is withdrawn from the fractionation zone as it is produced and may be recycled to the reaction zone for further conversion or yielded as a product from the process.

In the development of the fluid catalytic cracking process, it has been found that recycle stocks are more refractory and thus more difficult to convert than virgin stocks. To obtain a more desirable product distribution these more refractory recycle stocks may be cracked under more severe conditions than the virgin stocks.

Advantageously, two risers may be employed in the fluidized catalytic cracking process. Preheated virgin hydrocarbon stock and regenerated catalyst from the regeneration zone are charged into a first riser. An optimum conversion of virgin stock into desired products may be obtained by regulating the reaction conditions within the first riser. The first riser discharges into the reaction vessel at an intermediate point located such that the discharged hydrocarbon is contacted with the catalyst inventory for a desired relatively short period. For example, the discharge from the first riser may be deflected downward and such discharge may be located immediately above the surface of a fluidized dense phase catalyst bed which exists in the reactor vessel. By this means the downwardly directed hydrocarbon discharge from the first riser is contacted with the catalyst inventory of the reactor vessel for only a short period. Cycle gas-oil recycle from the fractionation zone and regenerated catalyst may be charged into a second riser. Reaction conditions in the second riser for the conversion of the recycle stock are relatively more severe than the reaction conditions employed for the virgin stock in the first riser. The second riser may discharge into the reactor vessel at a point below the discharge of the first riser. Thus the recycle hydrocarbon discharged from the second riser will traverse a greater amount of the catalyst inventory in the reactor vessel than the hydrocarbon being discharged from the first riser. This additional contact of the recycle hydrocarbon with the catalyst in the reactor vessel increases the conversion of the recycle hydrocarbon.

In applying the method of the present invention to a fluid catalytic cracking process wherein separate risers are employed for the virgin hydrocarbon stock and for the recycle stock, a modification of the control method of the present invention may be employed. In one embodiment of the present invention, when applied to such a process, a gasoline and lighter fraction is applied withdrawn from the fractionation zone as it is produced, light cycle gas-oil is withdrawn at a selected rate, intermediate cycle gas-oil is recycled from the fractionation zone to the second riser at a set rate, and a level indicating means is employed to determine the cycle gas-oil liquid level in the accumulation section of the fractionation zone. The heavy cycle gas-oil fraction is also withdrawn from the fractionation zone as it is produced. Preferably, the reaction conditions in the first riser are maintained such as to obtain an optimum conversion of virgin stock into desired products. One method for obtaining this optimum conversion is to monitor the reaction temperature within the first riser and to adjust the regenerated catalyst to oil ratio to obtain the optimum conversion temperature for the virgin stock. Conversion of intermediate cycle gas-

oil recycle in the second riser is controlled by admission of regenerated catalyst from the regeneration zone into the second riser at a catalyst to oil ratio sufficient to maintain the liquid level of cycle gas-oil within the accumulation section of the fractionation zone. The fresh feed conversion rate is adjusted to obtain the desired product distribution between gas-oil and the lighter components. By employing this embodiment of the present invention, an optimum yield of desired products may be obtained from the virgin stocks upon a once through conversion basis and additional amounts of desired products in a selected product distribution may be obtained from the intermediate cycle gas-oil recycle.

The method of the present invention may be better understood by reference to the attached drawing which illustrates and exemplifies one embodiment of the method by which the present invention may be practiced. This embodiment is not intended to restrict the invention since many modifications may be made within the scope of the claims without departing from the spirit thereof.

Referring to the drawing, a preheated virgin gas-oil feed boiling in the range from 450° F. to 1050° F. from line **10** is contacted with hot regenerated catalyst from a standpipe **11** at a temperature of about 1080° F. in the inlet portion of fresh feed riser **12**. The resulting mixture of catalyst and oil vapor at a temperature of about 920° F., and an average velocity of about 40 feet per second providing a residence time of about 4 seconds passes upwardly through fresh feed riser **12** and into the reactor vessel **13** wherein the fresh feed riser **12** terminates in a downwardly directed outlet. The catalyst to oil weight ratio in the fresh feed riser is about 9.8 to 1. Substantial conversion of the fresh feed occurs in the fresh feed riser **12** and at these conditions about 30 volume percent of the fresh feed is converted to products boiling below 430° F. The desired reaction temperature within the upper portion of the fresh feed riser **12** is obtained by employing temperature responsive means **15** to adjust a slide valve **19** to control the amount of regenerated catalyst admitted from a regeneration zone **20** into the fresh feed riser **12**. The slide valve **19** controls the amount of regenerated catalyst which enters the fresh feed riser **12** to such a rate that a desired reaction temperature in the upper portion of fresh feed riser **12** is maintained. Regenerated catalyst from the regenerator **20** passes through standpipe **52**, through slide valve **19** into standpipe **11**. From standpipe **11** the regenerated catalyst enters the fresh feed riser **12**. Intermediate cycle gas-oil recycle is introduced via line **21** into the inlet section of recycle riser **22** wherein it is contacted with regenerated catalyst at a temperature of about 1080° F. from a second standpipe **23**. The resulting catalyst-recycle vapor mixture at a temperature of 950° F. passes upwardly through the recycle riser **22** at an average velocity of about 30 feet per second with an average residence time of about 5 seconds. Other conditions in the recycle riser include a catalyst to oil weight ratio of about 10.2 to 1 and a weight hourly space velocity of 45. About 60 volume percent of the recycle is converted to products boiling below 430° F. in the recycle riser **22**.

The recycle riser **22** terminates in a downwardly directed outlet which discharges into the reactor vessel **13**. The hydrocarbon vapor effluent of the recycle riser **22** discharges into the reactor vessel **13** and passes upwardly through the fluidized catalyst dense phase bed in the reactor **13** effecting further conversion of the recycle into about 74.5 percent of products boiling below 430° F. Reaction conditions in the fluidized bed in reactor **13** include a temperature of 940° F. and a weight hourly space velocity of 12.8. The combined fresh feed riser cracking, recycle riser cracking, and reactor bed cracking provide an overall conversion of about 65.2 volume percent of the fresh feed into products boiling below 430° F. and a light cycle gas-oil yield of 24.6 volume percent basis fresh feed. Vapor velocities in the reactor vessel **13** are 1.5 feet per second at the point at which the recycle riser **22** discharges, 3.3 feet per second at the point where the fresh feed riser **12** discharges and 1.6 feet per second in the upper portion above the fluidized catalyst bed.

Vaporized products disengage from the dense phase catalyst bed at level **25** at a vapor velocity of about 0.8 feet per second. The vapors and any entrained catalyst, pass through a cyclone **26** wherein entrained catalyst is separated and returned to the catalyst bed through dipleg **27**. Although only one cyclone is shown it will be understood that several cyclones may be assembled in series to achieve substantially complete separation and a plurality of such assemblies may be employed to handle the volume of vapor encountered. Effluent vapors pass from cyclone **26** through line **28** into plenum chamber **29** wherein gases from other cyclone assemblies, not shown, are collected and discharged from the reactor vessel **13** through line **30**. The vapor line **30** conveys reaction products to a fractionation column **54** as will hereinafter be further described.

Steam from line **31** is passed to steam ring **32** and discharged into the lower portion of the reactor vessel **13** at a point below the outlet of the recycle riser **22**. Dense phase fluidized catalyst in the lower portion of the reactor **13** is stripped by such steam and passes downwardly through the standpipe **33** and catalyst valve **34** into a stripping zone **35**. Steam from line **37** is discharged through steam ring **38** into the lower portion of the stripper **35**. Steam rising through the stripper **35** removes occluded and entrained hydrocarbon vapors from the catalyst. The steam and removed hydrocarbon vapors pass upwardly through stripper vent line **39** discharging into the upper portion of the reactor vessel **13**.

Stripped catalyst is withdrawn from the bottom of the stripper **35** through spent catalyst standpipe **40** at a rate controlled by a slide valve **41** and discharges through stand pipe **42** into the regenerator **20**. In regenerator **20** the spent catalyst is contacted with air introduced through line **43** and air ring **44**. Oxygen from the air burns acculated coke from the stripped catalyst thereby regenerating the catalyst. Catalyst undergoing regeneration in the regenerator **20** forms a fluidized dense phase bed having a top level **45**. Flue gas resulting from the combustion of coke passes upwardly and enters cyclone **46** wherein entrained catalyst is separated and returned to the dense phase bed through dipleg **47**. Cyclone **46** although represented as a single vessel may, of course, comprise an assembly of cyclones arranged in parallel and in series to effect substantially complete separation of entrained solids from the flue gas. Effluent gas from the cyclone **46** passes through line **48** into plenum chamber **49** and outwardly through flue gas line **50** to vent facilities not shown. Regenerated catalyst is withdrawn from the bottom of the regenerator **20** through standpipes **51** and **52** at rates controlled by slide valves **19** and **53** to supply the hot regenerated catalyst to standpipes **11** and **23** as described above.

Product vapor in line **30** passes from the reactor vessel **13** to a fractional distillation column **54** wherein the product vapor is fractionated into desired component fractions. A vapor fraction comprising gasoline and lighter hydrocarbons is recovered overhead from the fractional distillation column **54** via line **55**. From line **55** the vapor fraction passes into condenser **56** wherein substantially all of the gasoline is condensed. From the condenser **56**, condensate and noncondensed vapors flow via line **57** into an accumulator vessel **58**, wherein the noncondensed vapors separate from the condensate. The noncondensed vapors comprising material lighter than gasoline are recovered from the accumulator **58** via line **59** and are transferred to further treating, not shown. A portion of the condensate comprising gasoline is passed from the accumulator **58** via line **60** as overhead reflux to the fractional distillation column **54**. Product gasoline is

withdrawn from the accumulator vessel **58** via line **61** and is passed to further treating, not shown. Water, which comprises condensed stripping steam from the reactor vessel **13** collects in the accumulator vessel dipleg **62** from which it is removed via line **63**.

A liquid fraction comprising light cycle gas-oil is withdrawn from the fractional distillation column **54** via line **64** through which the light cycle gas-oil is passed to storage, not shown. A selected light cycle gas-oil withdrawal rate is maintained by a flow responsive control means **65**.

A heavy cycle gas-oil fraction is withdrawn from the bottom of the fractional distillation column **54** via line **66**.

Within the fractional distilaltion column **54** a liquid fraction comprising intermediate cycle gas-oil accumulates upon a trap tray **67**. From the trap tray **67** a recycle stream comprising intermediate cycle gas-oil is withdrawn via line **68** at a set rate controlled by flow responsive control means **69**. From the flow responsive control means **69** the gas-oil recycle steam, at a temperature of about 630° F. passes via line **21** to the inlet section of the recycle riser **22** as hereinbefore described. The temperature at which the intermediate cycle gas-oil recycle stream is transferred is about the boiling point temperature of the intermediate cycle gas-oil fraction accumulated upon the trap tray **67**. If desired, an intermediate cycle gas-oil product slip stream may be recovered from line **68** via line **71** through which the intermediate cycle gas-oil slip stream passes to storage, not shown.

The level **72** of accumulated gas-oil upon the trap tray **67** is maintained by controlling the conversion of intermediate cycle gas-oil recycle in the recycle riser **22**. A level responsive control means **70** adjusts the slide valve **53** through which regenerated catalyst enters the recycle riser **22** via the standpipe **23**. The degree of conversion of recycle in the recycle riser **22** is determined by the ratio of regenerated catalyst to recycle in the recycle riser **22**. Thus, for example, by increasing the catalyst to oil ratio in the recycle riser, the conversion of intermediate cycle gas-oil recycle is increased and the amount of unconverted recycle returning to the trap tray decreases. Since the intermediate cycle gas-oil recycle rate is set, the level **72** will then descend.

The product distribution between gasoline and lighter hydrocarbons may be adjusted by the proper selection of the intermediate cycle gas-oil recycle rate. In order to maintain a material balance within the fluidized catalytic cracking process, intermediate cycle gas-oil must be consumed at the net rate at which it is produced and accumulates upon the trap tray **67**. Thus, the amount of intermediate cycle gas-oil recycle which must be converted per pass through the reaction zone is determined by the net rate of heavy cycle gas-oil accumulation upon the trap tray **67**. At relatively high recycle rates the fraction of the recycle stream which must be converted per pass through the reaction system in order to maintain the system balance is small. Thus relatively mild cracking conditions in the recycle riser may be employed. Under relatively mild cracking conditions the proportion of light cycle gas-oil to lighter hydrocarbons is increased.

However, at relatively low recycle rates the fraction of the recycle stream which must be converted per pass in order to maintain a system balance is increased, and more severe cracking conditions are required to increase the fraction of the recycle stream converted. Under more severe cracking conditions, the conversion of recycle to lighter hydrocarbons is increasingly favored at the expense of the light cycle-gas-oil component. Thus, by properly selecting the intermediate cycle gas-oil recycle rate a range of product distribution between light cycle gas-oil, gasoline, and lighter components may be obtained.

As will be apparent to those skilled in the art in light of the foregoing disclosure many modifications and changes are possible in the practice of this invention without departing from the spirit and scope thereof.

I claim:

1. In a fluidized catalytic cracking process for the conversion of hydrocarbon into desirable products wherein fresh feed hydrocarbon is converted by contact with hot catalyst in a fresh feed riser, wherein intermediate cycle gas-oil recycle is converted by contact with hot catalyst in a recycle riser, wherein hydrocarbon product vapors are separated from the catalyst subsequent to the conversion step, wherein product vapors are fractionated in a fractional distillation zone into at least a gasoline and lighter fraction, a light cycle gas-oil fraction and a recycle fraction; the improvement for maintaining a desired product distribution of converted hydrocarbon which comprises:

(a) recovering from the fractional distillation zone a light cycle gas-oil fraction at a selected rate;

(b) accumulating a quantity of recycle fraction in an accumulation section of the fractional distillation zone;

(c) recycling the recycle fraction from the accumulation section of the fractional distillation zone to the recycle riser at a set rate; and

(d) adjusting the addition of hot catalyst to the recycle riser to maintain the quantity of recycle fraction in the accumulation section of the fractional distillation zone.

2. The method of claim **1** wherein the recycle rate of the recycle fraction is set to obtain a desired product distribution between light cycle gas-oil and lighter hydrocarbons.

3. The method of claim **2** wherein the addition of regenerated catalyst to the reaction zone is controlled by a means responsive to the level of accumulated intermediate cycle gas-oil in the accumulation section.

References Cited

UNITED STATES PATENTS

3,175,968	3/1965	Berger	208—164
3,630,886	3/1970	Deed et al.	208—96
3,316,170	4/1967	Stewart et al.	208—164
3,619,415	11/1971	Jones et al.	208—164

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