

**SYSTEM AND METHOD FOR SELECTIVE COMPONENT CRACKING
TO MAXIMIZE PRODUCTION OF LIGHT OLEFINS**

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application claims priority to U.S. provisional application Serial No. 60/538,906 filed January 23, 2004, which is herein incorporated by reference in its entirety.

BACKGROUND

1. Field of the Invention

The present invention relates to a system and method for fluid catalytic cracking (FCC) to maximize the yield of light olefins.

2. Background of the Art

The fluid catalytic cracking (FCC) process is commonly used to crack high boiling petroleum fractions by contacting the high boiling feed with fluidized catalyst particles in a riser to produce primarily motor fuels. It also produces a certain amount of light hydrocarbons such as C₃ and C₄ compounds and light olefins such as propylene and butylenes. However, the relative demand for the light olefins has been increasing. Therefore, the FCC process needs to be adapted to produce more of these light olefins.

For example, U.S. Patent No. 5,997,728 discloses a catalyst system for maximizing light olefin yields in FCC. The process employs a catalyst with large amounts of shape selective cracking additive.

U.S. Patent No. 6,069,287 discloses a process for selectively producing C₂-C₄ olefins in a FCC process from a thermally cracked naphtha stream. The naphtha stream is contacted with a catalyst containing from about 10 to 50

wt% of crystalline zeolite having an average pore diameter of less than about 0.7 nanometers.

U.S. Patent No. 6,093,867 discloses a process for selectively producing C₃ olefins from a catalytically cracked or thermally cracked naphtha stream. The naphtha stream is introduced into a process unit comprised of a reaction zone, a stripping zone, a catalyst regeneration zone, and fractionation zone. The naphtha feed stream is contacted in the reaction zone with a catalyst containing from about 10 to 50 wt. % of a crystalline zeolite having an average pore diameter less than about 0.7 nanometers at reaction conditions which include temperatures ranging from about 500° to 650° C. and a hydrocarbon partial pressure from about 10 to 40 psia. Vapor products are collected overhead and the catalyst particles are passed through the stripping zone on the way to the catalyst regeneration zone. Volatile compounds are stripped with steam in the stripping zone and the catalyst particles are sent to the catalyst regeneration zone where coke is burned from the catalyst, which is then recycled to the reaction zone. Overhead products from the reaction zone are passed to a fractionation zone where a stream of C₃'s is recovered and a stream rich in C₄ and/or C₅ olefins is recycled to the stripping zone.

Other patents describing FCC processes for producing higher yields of light olefins include U.S. Patent Nos. 6,106,697, 6,118,035, 6,313,366 and 6,538,169, for example.

There is yet a need for a FCC system and method that is able to maximize production of light olefins more efficiently and selectively.

SUMMARY

A process for the fluid catalytic cracking of hydrocarbons is provided herein. The process comprises contacting a feed of heavy/high boiling

hydrocarbons with a particulate catalyst in a reaction zone under fluidized catalytic cracking conditions to convert at least some of the hydrocarbons to light olefins having from 3 to 4 carbon atoms, conveying spent catalyst and a gaseous fluid containing the light olefins and other products of conversion to a cyclone separation system within a containment/separation vessel, the containment/separation vessel enclosing an interior space having a stripping region and an upper region in which the cyclone separation system that is directly connected to the riser reaction zone is positioned, wherein the cyclone separation system includes a first cyclone having an interior first pressure and said stripping region having a second pressure, the interior first pressure being at least about 0.05 psi lower than the stripping region second pressure. The gaseous hydrocarbon products are separated from the catalyst particles in the cyclone separation system and flow to the product separation or fractionation section downstream of the separation vessel. The catalyst particles are then transferred to the stripping region. The spent catalyst particles are contacted with a stripping gas to remove entrained hydrocarbons, the stripping gas with entrained hydrocarbons being moved through the cyclone and through the exit port. The stripped catalyst particles are then transferred to a regeneration zone for decoking, and the decoked or regenerated catalyst particles are then transferred back to the reaction zone.

BRIEF DESCRIPTION OF THE DRAWINGS

Various embodiments are described below with reference to the drawings wherein:

FIG. 1 is a schematic illustration of reactions occurring in an FCC process;

FIG. 2 is a diagrammatic illustration of an FCC system employing the invention employing a single riser reaction zone;

FIG. 3 is a diagrammatic illustration of an alternative FCC system employing dual riser reaction zones;

5 FIG. 4 is a graph illustrating pressure differential versus product recovery efficiency; and,

FIG. 5 is a graph illustrating C_3H_6 selectivity versus feed conversion.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT(S)

10 The FCC process of the invention employs a catalyst in the form of very fine solid particles that are fluidized in a reaction zone which is in the form of a vertical riser reactor. The feed is contacted with the catalyst at the bottom of the vertical riser reactor and lifted with the catalyst to the top of the riser reactor, as described more fully below.

15 The feed is a relatively heavy hydrocarbon fraction having a relatively high boiling point and/or molecular weight. The term "relatively heavy" as used herein refers to hydrocarbons having five or more carbon atoms, typically more than 8 carbon atoms. For example, the feed can be a naphtha, vacuum gas oil or residue. Typically, the feed is a petroleum fraction having a boiling range of
20 from about 250°C to about 625°C.

 The catalyst used in this invention can be any catalyst commonly used in FCC processes. These catalysts generally consist of high activity crystalline alumina silicates. The preferred catalyst components are zeolites, as these exhibit higher intrinsic activity and resistance to deactivation. Typical zeolites
25 include ZSM-X, ZSM-Y, ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38 and ZSM-48. A more preferred catalyst of the present invention is based upon Ultrastable Y (USY) zeolite with higher silica to alumina ratio. The catalysts can

be used alone or in combination with zeolites having a shape selective pentasil structure, such as ZSM-5, that convert larger linear hydrocarbon compounds to smaller ones, especially larger olefins to smaller olefins. Non-zeolite catalysts such as amorphous clays or inorganic oxides can also be employed.

5 The present invention maximizes selectivity of the light olefins (C_3 - C_4 olefins) by means of the FCC unit hardware design, operating conditions and catalyst formulation. The hardware design, operating conditions, and catalyst formulation are tailored to achieve kinetic and thermodynamic effects which favor the production of olefins. The catalyst formulation or the mixture of
10 catalysts used in this invention is selected from the family of catalysts described above, such that the catalysts activity for catalytic conversion is maximized along with maximization of conversion of larger molecular weight olefins to smaller molecular weight olefins, while the tendency for resaturation of the light olefins thus produced is minimized.

15 Referring to FIG. 1, various reactions which occur in FCC are diagrammatically illustrated. Paraffins are cracked to produce olefins. Olefins, however, can react to produce naphthenes through cyclization reactions, smaller olefins through cracking reactions, and paraffins through hydrogen transfer. Olefins can also undergo isomerization. The naphthenes can be
20 converted to olefins or cycloolefins. Aromatics can be produced by dehydrogenation of cycloolefins. The aromatics, in turn, can be cracked, or can undergo dehydrogenation and/or alkylation to produce heavy coke, and polycyclic or heterocyclic aromatics.

25 The desired reaction is the conversion of paraffins to light olefins, which is characterized by a faster reaction rate than the undesired secondary reactions. Thus, by limiting the reaction time, one can terminate the undesired chain reactions quickly after the olefin production has taken place. The quick

termination of the side reactions is achieved by having a very short residence time in the riser reactor and, more importantly, quick and efficient separation of the reaction products from the catalyst at the termination of the reaction at the end of the riser reactor.

5 Referring now to FIG. 2, a FCC system 100 is illustrated for the selective component cracking of the invention. The system 100 includes a vertical riser reactor 101. The initial feed is introduced into the riser 101 through injectors 102. Regenerated catalyst mixes with the feed and both are carried upward in the riser wherein the cracking reaction occurs.

10 Regenerated catalyst typically enters the riser at a temperature of about 650°C to 760°C and the cracking reaction in the riser usually occurs at a temperature in the range of about 500°C to about 600°C.

Low hydrocarbon partial pressure in the riser favors light olefin production. Generally, the riser pressure is set at about 10 to 25 psig, with a hydrocarbon partial pressure of about 3 to 10 psig. Steam or other dry gas may
15 be used as a diluent to achieve the lower hydrocarbon partial pressure.

In order to maximize the production of light olefins, certain selected components of the product of the first pass conversion are recycled to the riser reactor for further cracking. This mode of operation is termed selective
20 component cracking ("SCC"). The selected component to be recycled and re-cracked could be a range of materials such as higher carbon number olefins, or straight run products from other conversion units. The selected components are not mixed with the fresh feed at injector 102. Rather, these components are injected separately through a set of injection points in the riser reactor system
25 where the conditions are ideal for cracking these components. The lighter selected components are injected through multiple injectors 103a upstream of

the fresh feed injector 102 and at points where these components can thoroughly mix or contact the high activity, high temperature catalyst.

Optimization of the reaction residence time is an important feature of the invention. Longer residence time allows for more thorough cracking, but also increases the secondary reactions that reduce the yield of light olefins. Preferred residence times range from 0.5 to 10.0 seconds, more preferably 1.0 to 5.0 seconds and most preferably 1.0 to 3.0 seconds.

The reactor effluent exits at the top of riser 101 and enters separator vessel 110 and is introduced into at least one, and preferably two, cyclone separators. The gas and solids are mostly separated in first cyclone 111, and the overhead from first cyclone 111 is directed to second cyclone 112 for final separation. The solids drop out through diplegs 113 into the stripper 114. The gases are sent out through outlet 118 to a main, or primary, fractionation column and downstream product separation system where various product fractions are separated through a number of fractionation steps. Some of the products are recycled back to the reaction, as mentioned above.

A unique feature applied in this invention that helps to preserve the yield of light olefins formed in the riser reaction zone is that the cyclone 111 operates at a lower pressure than the interior of the vessel 110. This pressure differential is maintained by having the gases from the stripper vessel 114 pass through an orifice in the roof of the cyclone 111, as described, for example, in U.S. Patent No. 5,248,411, which is herein incorporated by reference. The lower pressure in cyclone 111 provides complete separation of the reacting hydrocarbons from the catalyst so as to quickly terminate secondary chain reactions, and thereby preserves the yield of light olefins. Referring now to FIG. 4, it can be seen that when cyclone 111 are operating at a negative pressure, i.e., when the pressure in cyclone 111 is lower than the pressure in vessel 110,

the product recovery efficiency is almost 100%. When the pressure differential is zero, i.e., when vessel 110 and cyclone 111 are at the same pressure, the efficiency of product recovery is 97%. When cyclone 111 is at a pressure only 0.4 psi higher than the pressure in vessel 110, the product recovery efficiency drops to below 80%. The lower cyclone pressure prevents the reacting gases from flowing down with the separated catalyst solids through the diplegs and into the interior of vessel 110. Otherwise, the reacting gases would remain in contact with the catalyst and the slower secondary reactions would have additional time to proceed and reduce selectivity for olefins.

During the course of reaction in the riser reactor 101, the catalyst particles become laden with predominantly carbonaceous material termed "coke" that is a by-product of the cracking reactions. The catalyst particles also contain hydrocarbons in their pores and entrain some hydrocarbons after separation from the vapor phase in the cyclones 111 and 112. The coke deposits deactivate the catalyst by blocking active access of the reacting species to the active sites of the catalyst. The catalyst activity is restored by combusting the coke with an oxygen-containing gas in a regeneration vessel 120. However, before the regeneration step, the catalyst is stripped with steam in the stripping vessel 114 to remove the accompanying hydrocarbon vapors that would, otherwise, burn in the regenerator and represent loss of the valuable products.

Referring now again to FIG. 2, the catalyst particles which flow out of the cyclones 111 and 112, fall into the stripping section 114 of vessel 110 wherein the particles are separated of any entrained or adsorbed hydrocarbons by conventional countercurrent contact with steam. The stripper internals are designed to maximize contact time and surface area for mass transfer between the fluidized catalyst phase and the stripping steam phase. The stripped catalyst particles then drop through downflow line 115 and are carried by

transfer line 116 to a square bend 117 from which they are carried upward into the middle of fluid bed 121 in regenerator 120 through outlet 122. Uniform distribution of the coke laden catalyst in the center of the regeneration bed 121 is important for regaining catalyst activity and surface area. The square bend transfer line possesses a unique configuration that eliminates erosion problems associated with other designs for similar dilute phase catalyst transfer, such as the use of an elbow for the horizontal to vertical turn for the transport of the spent catalyst. This square bend configuration results in trouble-free introduction of the spent catalyst into the center of the regenerator for uniform and thorough regeneration of the catalyst, so that catalyst activity for desired reactions is maximized for the production of light olefins.

Oxygen containing gas, e.g., air, is introduced in the regenerator 120 through inlet 123 under bed 121 to fluidize the bed and to oxidize coke deposits on the catalyst particles through combustion. Combustion gas inlet 123 is representative of a plurality of such distributors such that the oxygen containing gas is spread uniformly across the bed area so as to match the distribution of the spent catalyst from the outlet 122. The exhaust resulting gas is sent through cyclones to separate out any catalyst particles and then through outlet 128.

Regenerated (i.e., decoked) catalyst particles are then withdrawn through line 131 and flow down through regenerated catalyst standpipe 130 and via regenerated catalyst feed line 133, into the riser 101. Line 132 serves as a vent to facilitate downflow of the catalyst particles.

Referring now to FIG. 3, an alternative embodiment 200 of the FCC system is illustrated. System 200 is similar to system 100 except that it includes a second riser reactor 201. Initial feed is introduced into riser 201 through injector 202. Selected components recycled from the first pass

conversion can be introduced into the riser 201 at injector 203a. Regenerated catalyst from regenerated catalyst standpipe 130 is introduced into riser 201 via regenerated catalyst feed line 233. The effluent from riser reactor 201 exits at the top of the riser and is introduced into a first cyclone 211. The overhead from the first cyclone is introduced into a second cyclone 212. The solids drop through the cyclone diplegs into the stripping region 114. As described above, the pressure inside cyclones 211 and 212 is less than the pressure within stripping region 114.

Referring now to Fig. 5, the relationship between propylene selectivity and feed conversion with parameters of hydrocarbon partial pressure is illustrated. The graph shows the advantage of operating the FCC process at a lower hydrocarbon partial pressure. For hydrocarbon partial pressure X, wherein X can range from about 10 psig to about 25 psig, it can be seen that a decrease of hydrocarbon partial pressure of 5 psig (X-5 psi) results in dramatically improved selectivity to propylene. Accordingly, it is a feature of the invention to conduct the FCC process at a hydrocarbon partial pressure of no more than about 10 psig, preferably no more than about 7 psig and more preferably no more than about 5 psig.

While the above description contains many specifics, these specifics should not be construed as limitations of the invention, but merely as exemplifications of preferred embodiments thereof. Those skilled in the art will envision many other embodiments within the scope and spirit of the invention as defined by the claims appended hereto.

WHAT IS CLAIMED IS:

1. A process for the fluid catalytic cracking of hydrocarbons comprising:

a) contacting a primary feed of relatively heavy hydrocarbons with a fluidized particulate catalyst in a reaction zone under catalytic cracking conditions to convert at least some of the heavy hydrocarbons to light olefins having from 3 to 4 carbon atoms;

b) conveying a reaction mixture containing spent catalyst particles and a gaseous stream containing the light olefins and other reaction products to a cyclone separation system directly connected to the reaction zone, at least part of said cyclone separation system being positioned within an interior space enclosed by a vessel, said interior space including a stripping region and an upper region in which the at least part of the cyclone separation system is positioned, said cyclone separation system including at least one cyclone connected directly to the reaction zone and having an interior first pressure and said stripping region having a second pressure, said interior first pressure being at least 0.05 psig lower than the second pressure;

c) separating the spent catalyst particles from the gaseous fluid within said at least one cyclone, said gaseous fluid being ejected as effluent from the separation vessel through an exit port and said spent catalyst particles being transferred to the stripping region; and,

d) contacting said spent catalyst particles with a stripping gas to remove entrained hydrocarbons, said stripping gas with entrained hydrocarbons being moved through the at least one cyclone through the exit port.

2. The process of claim 1 further including the step:

e) transferring the stripped catalyst particles to a regeneration zone for decoking.

5 3. The process of claim 2 further including the step:

f) decoking at least a portion of the stripped catalyst to provide regenerated catalyst.

10 4. The process of claim 1 wherein the catalyst comprises one or more zeolitic material selected from the group consisting of USY, ZSM-X, ZSM-Y, ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38 and ZSM-48.

15 5. The process of claim 1 wherein the hydrocarbon feed comprise a petroleum fraction having a boiling range of from about 250°C to about 625°C.

6. The process of claim 1 wherein the catalytic cracking conditions include a temperature of from 500°C to about 600°C, a pressure of from about 10 to 25 psig, a residence time of from about 0.5 seconds to about 10.0 seconds and a hydrocarbon partial pressure of from about 3 psig to about 10 psig.

20 7. The process of claim 1 further comprising the step of injecting at least a second feed component into said reaction zone separately from said primary feed, said second feed component comprising a recycled portion of the effluent from the separation vessel, said recycled portion of the effluent being separated
25 from the effluent downstream of the separation vessel by fractionation.

8. The process of claim 1 wherein the reaction zone comprises a vertically oriented riser reactor wherein the primary feed is introduced into the riser reactor at a position in the vicinity of a bottom portion of the riser reactor and exits the reaction zone at a top portion of the riser reactor.

9. The process of claim 7 wherein the second feed component comprises a hydrocarbon fraction which is lighter than the saturated hydrocarbons of the primary feed and which is introduced in the riser reactor through multiple points downstream of the position at which the primary feed is introduced.

10. The process of claim 3 wherein the step of transferring the stripped catalyst particles to a regeneration zone comprises conducting the catalyst particles through a square bend transfer line.

11. The process of claim 10 wherein the regeneration zone includes a fluidized bed and the stripped catalyst particles are introduced in the vicinity of the center of the fluidized bed.

12. The process of claim 11 wherein the decoking step includes contacting the stripped catalyst particles in the fluidized bed of the regeneration zone with an oxidizing gas.

13. The process of claim 12 further comprising the step of:
transferring at least a portion of regenerated catalyst to the reaction
zone.

5 14. The process of claim 13 wherein the transferred portion of
regenerated catalyst is conducted through a stand pipe and recycled to the
reaction zone.