

**RECRACKING MIXTURES OF CYCLE OIL AND CAT
NAPHTHA FOR MAXIMIZING LIGHT OLEFIN YIELDS**

FIELD OF THE INVENTION

- 5 **[0001]** This invention relates to a fluid catalytic cracking process. More particularly, a mixture of cycle oil, light cat naphtha, and steam are added to the reaction zone to improve yields of light olefins.

BACKGROUND OF THE INVENTION

- 10 **[0002]** Fluid catalytic cracking (FCC) is a well-known method for converting high boiling hydrocarbon feedstocks to lower boiling, more valuable products. In the FCC process, the high boiling feedstock is contacted with fluidized catalyst particles in the substantial absence of hydrogen at elevated temperatures. The cracking reaction typically occurs in the riser portion of the catalytic cracking reactor. Cracked products are separated from catalyst by means of cyclones and coked catalyst particles are
15 steam-stripped and sent to a regenerator where coke is burned off the catalyst. The regenerated catalyst is then recycled to contact more high-boiling feed at the beginning of the riser.

- 20 **[0003]** Typical FCC catalysts contain active crystalline aluminosilicates such as zeolites and active inorganic oxide components such as clays of the kaolin type dispersed within an inorganic metal oxide matrix formed from amorphous gels or sols that bind the components together on drying. It is desirable that the matrix be active, attrition resistant, selective with regard to the production of hydrocarbons without excessive coke make and not readily deactivated by metals. Current FCC catalysts may contain in excess of 40 wt.% zeolites.

- 25 **[0004]** There is a growing need to utilize heavy streams as feeds to FCC units because such streams are lower cost as compared to more conventional FCC feeds such

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together with high levels of metals such as sodium, iron, nickel and vanadium. Nickel and vanadium may lead to excessive "dry gas" production during catalytic cracking. Vanadium, when deposited on zeolite catalysts can migrate to and destroy zeolite catalytic sites. High con carbon feeds lead to excessive coke formation. These factors result in FCC unit operators having to withdraw excessive amounts of catalyst to maintain catalyst activity. This, in turn, leads to higher costs from fresh catalyst make-up and deactivated catalyst disposal.

[0005] U.S. 4,051,013 describes a cat cracking process for simultaneously cracking a gas oil feed and upgrading a gasoline-range feed to produce high quality motor fuel. The gasoline-range feed is contacted with freshly regenerated catalyst in a relatively upstream portion of a short-time dilute-phase riser reactor zone maintained at first catalytic cracking conditions and the gas oil feed is contacted with used catalyst in a relatively downstream portion of the riser reaction zone which is maintained at second catalytic cracking conditions. U.S. 5,043,522 relates to the conversion of paraffinic hydrocarbons to olefins. A saturated paraffin feed is combined with an olefin feed and the mixture contacted with a zeolite catalyst. The feed mixture may also contain steam. U.S. 4,892,643 discloses a cat cracking operation utilizing a single riser reactor in which a relatively high boiling feed is introduced into the riser at a lower level in the presence of a first catalytic cracking catalyst and a naphtha charge is introduced at a higher level in the presence of a second catalytic cracking catalyst. U.S. 5,846,403 discloses an FCC reaction wherein a mixture of light catalytically cracked naphtha ("light cat naphtha" or "LCN") and steam is injected into an FCC riser at a point upstream of gas oil or residual oil injection. Such LCN and steam coinjection results in augmented light olefin production in the FCC unit.

[0006] It would be desirable to have improved FCC processes capable of increasing light olefin yield while at the same time reducing dry gas.

SUMMARY OF THE INVENTION

[0007] It has been discovered that adding a mixture of cycle oil, light cat naphtha, and steam to an upstream reaction zone in an FCC process results in improved light olefin yields compared to base operation and a decrease in dry gas compared to neat light cat naphtha recycle. Accordingly, the present invention relates to a fluid catalytic cracking process for upgrading feedstocks to increase yields of C₃ and C₄ olefins, the process comprising:

conducting hot regenerated catalyst to an FCC unit having at least one riser reactor containing a downstream and an upstream reaction zone;

contacting hot catalyst with a cycle oil, a light cat naphtha, and steam in the upstream reaction zone at a temperature of from about 620 to 775°C and a vapor residence time of cycle oil, naphtha, and steam of less than 1.5 sec. wherein at least a portion of the C₅ to C₉ olefins present in the light cat naphtha is cracked to C₃ and C₄ olefins and wherein at least a portion of the cycle oil's saturated species are converted into lower boiling point products including C₂ to C₅ olefins;

contacting the catalyst, cracked cycle oil products, and cracked naphtha products, and steam from the upstream reaction zone with a heavy feedstock in the downstream reaction zone at an initial temperature of from about 600 to 750°C with vapor residence times of less than about 20 seconds;

conducting spent catalyst, cracked products and steam from the first and second reaction zones to a separation zone;

separating from the cracked products a cycle oil fraction, a light cat naphtha fraction, and steam from spent catalyst and recycling at least a portion of the cycle oil fraction and light cat naphtha fraction to the upstream reaction zone in step (b);

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conducting spent catalyst to a stripping zone and stripping spent catalyst under stripping conditions; and

conducting stripped spent catalyst to a regeneration zone and regenerating spent catalyst under regeneration conditions.

- 5 [0008] In another embodiment, the invention is related to a product formed in accord with such a process.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Figure 1 is a flow diagram showing the two zone feed injection system in the riser reactor.

- 10 [0010] Figure 2 shows the selectivity for olefins compared to dry gas for various LCN:cycle oil ratios.

DETAILED DESCRIPTION OF THE INVENTION

- [0011] The invention is based on the discovery that increased C₃ and C₄ olefin production over conventional (i.e., base) FCC operation and decreased dry gas production compared to neat LCN recycle in an FCC process may be obtained by
15 injecting cycle oil, LCN, and steam at a point upstream of heavy feed injection. More particularly, the invention is related to an FCC riser reactor having at least one two-zone riser reactor wherein cycle oil, LCN, and steam are injected into a second zone upstream of a first zone, the heavy feed being injected into the first zone.

- 20 [0012] The riser reactor of a typical FCC unit receives hot regenerated catalyst from the regenerator. Fresh catalyst may be included in the catalyst feed to the riser reactor. A lift gas such as light hydrocarbon vapors, or steam may be added to the riser reactor to assist in fluidizing the hot catalyst particles. In the present process, cycle oil,

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light cat naphtha, and steam are added in an upstream zone of the riser reactor. The cycle oil may include heavy cycle oil, light cycle oil, and mixtures thereof. Heavy cycle oil refers to a hydrocarbon stream boiling in the range of 240°C to 370°C (about 465°F to about 700°F). Light cycle oil refers to a hydrocarbon stream boiling in the range of 190°C to 240°C (about 375°F to about 465°F). Light cat naphtha refers to a hydrocarbon stream having a final boiling point less than about 150°C (300°F) and containing olefins in the C₅ to C₉ range, single ring aromatics (C₆ - C₉) and paraffins in the C₅ to C₉ range. Cycle oil and light cat naphtha ("LCN") is injected into the upstream reactor zone together with 2 to 50 wt.% of steam, based on total weight of cycle oil and LCN. The cycle oil, LCN, and steam have a vapor residence time in the upstream zone of less than about 1.5 sec., preferably less than about 1.0 sec, and more preferably less than 0.5 seconds. Cat/oil ratios range from 75 - 150 (wt/wt) at pressures of 100 to 400 kPa and temperatures in the range of 620 - 775°C. The addition of cycle oil, steam, and LCN in this upstream zone results in increased C₃ and C₄ olefins yields by cracking C₅ to C₉ olefins in the LCN feed and cracking principally saturated species in cycle oil to produce naphtha and lighter products.

[0013] Conventional heavy FCC feedstocks having a boiling point in the 220 - 575°C range such as gas oils and vacuum gas oils are injected in the downstream riser reaction zone. Small amounts (1-15 wt.%) of higher boiling fractions such as vacuum resids may be blended into the conventional feedstocks. Reaction conditions in the downstream reaction zone include initial temperatures of from 600-750°C and average temperatures of 525 - 575°C at pressures of from 100 - 400 kPa and cat/oil ratios of 4 - 10 (wt/wt) and vapor residence times of 2 - 20 seconds, preferably less than 6 seconds.

[0014] Suitable catalysts include any catalyst typically used to catalytically "crack" hydrocarbon feeds. It is preferred that the catalytic cracking catalyst comprise a crystalline tetrahedral framework oxide component. This component is used to catalyze

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the breakdown of primary products from the catalytic cracking reaction into clean products such as naphtha for fuels and olefins for chemical feedstocks. Preferably, the crystalline tetrahedral framework oxide component is selected from the group consisting of zeolites, tectosilicates, tetrahedral aluminophosphates (ALPOs) and tetrahedral
5 silicoaluminophosphates (SAPOs). More preferably, the crystalline framework oxide component is a zeolite.

[0015] Zeolites which can be employed in accordance with this invention include both natural and synthetic zeolites. These zeolites include gmelinite, chabazite, dachiardite, clinoptilolite, faujasite, heulandite, analcite, levynite, erionite, sodalite,
10 cancrinite, nepheline, lazurite, scolecite, natrolite, offretite, mesolite, mordenite, brewsterite, and ferrierite. Included among the synthetic zeolites are zeolites X, Y, A, L, ZK-4, ZK-5, B, E, F, H, J, M, Q, T, W, Z, alpha and beta, ZSM-types and omega.

[0016] In general, aluminosilicate zeolites are effectively used in this invention. However, the aluminum as well as the silicon component can be substituted for other
15 framework components. For example, the aluminum portion can be replaced by boron, gallium, titanium or trivalent metal compositions which are heavier than aluminum. Germanium can be used to replace the silicon portion.

[0017] The catalytic cracking catalyst used in this invention can further comprise an active porous inorganic oxide catalyst framework component and an inert catalyst
20 framework component. Preferably, each component of the catalyst is held together by attachment with an inorganic oxide matrix component.

[0018] The active porous inorganic oxide catalyst framework component catalyzes the formation of primary products by cracking hydrocarbon molecules that are too large to fit inside the tetrahedral oxide component. The active porous inorganic
25 oxide catalyst framework component of this invention is preferably a porous inorganic

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oxide that cracks a relatively large amount of hydrocarbons into lower molecular weight hydrocarbons as compared to an acceptable thermal blank. A low surface area silica (e.g., quartz) is one type of acceptable thermal blank. The extent of cracking can be measured in any of various ASTM tests such as the MAT (microactivity test, ASTM #D3907-8). Compounds such as those disclosed in Greensfelder, B. S., et al., Industrial and Engineering Chemistry, pp. 2573-83, Nov. 1949, are desirable. Alumina, silica-alumina and silica-alumina-zirconia compounds are preferred.

[0019] The inert catalyst framework component densifies, strengthens and acts as a protective thermal sink. The inert catalyst framework component used in this invention preferably has a cracking activity that is not significantly greater than the acceptable thermal blank. Kaolin and other clays as well as α -alumina, titania, zirconia, quartz and silica are examples of preferred inert components.

[0020] The inorganic oxide matrix component binds the catalyst components together so that the catalyst product is hard enough to survive interparticle and reactor wall collisions. The inorganic oxide matrix can be made from an inorganic oxide sol or gel which is dried to "glue" the catalyst components together. Preferably, the inorganic oxide matrix will be comprised of oxides of silicon and aluminum. It is also preferred that separate alumina phases be incorporated into the inorganic oxide matrix. Species of aluminum oxyhydroxides γ -alumina, boehmite, diaspore, and transitional aluminas such as α -alumina, β -alumina, γ -alumina, δ -alumina, ϵ -alumina, κ -alumina, and ρ -alumina can be employed. Preferably, the alumina species is an aluminum trihydroxide such as gibbsite, bayerite, nordstrandite, or doyleite.

[0021] Coked catalyst particles and cracked hydrocarbon products from the upstream and downstream reaction zones in the riser reactor are conducted from the riser reactor into the main reactor vessel which contains cyclones. The cracked

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hydrocarbon products are separated from coked catalyst particles by the cyclone(s). Coked catalyst particles from the cyclones are conducted to a stripping zone where strippable hydrocarbons are stripped from coked catalyst particles under stripping conditions. In the stripping zone, coked catalyst is typically contacted with steam.

5 Stripped hydrocarbons may be combined with cracked hydrocarbon products and recovered for storage or further processing.

[0022] After the coked catalyst is stripped of strippable hydrocarbon, the catalyst is then conducted to a regenerator. Suitable regeneration temperatures include a temperature ranging from about 1100 to about 1500°F (593 to about 816°C), and a

10 pressure ranging from about 0 to about 150 psig (101 to about 1136 kPa). The oxidizing agent used to contact the coked catalyst will generally be an oxygen-containing gas such as air, oxygen and mixtures thereof. The coked catalyst is contacted with the oxidizing agent for a time sufficient to remove, by combustion, at least a portion of the carbonaceous deposit and thereby regenerate the catalyst.

15 **[0023]** Referring now to Fig. 1, hot catalyst 10 from the regenerator (not shown) is conducted through regenerated catalyst standpipe 12 and slide valve 14 into the “J” bend pipe 16 which connects the regenerator standpipe 12 to the riser reactor 32. Lift gas 20 is injected into pipe 16 through injection nozzle 18 thereby fluidizing hot catalyst particles 10. Cycle oil and light cat naphtha 22 together with steam 24 are injected into

20 upstream reaction zone 34 through nozzle 26; multiple injection nozzles may be employed. In reaction zone 34, C₅ to C₉ olefins in the LCN are cracked to C₃ and C₄ olefins. Moreover, at least a portion of the saturated species present in the cycle oil is converted to lower boiling point products including light olefins. This reaction is favored by short residence times and high temperatures. Cracked hydrocarbon

25 products, partially deactivated catalyst and steam from reaction zone 34 are conducted to downstream reaction zone 36. In reaction zone 36, conventional heavy FCC

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feedstocks 28 are injected through multiple injection nozzles 30 and combined with the cracked hydrocarbon products, catalyst and steam from reaction zone. Residence times in zone 36 are longer which favor conversion of feed 28. Cracked products from zone 34 and 36 together with coked catalyst and steam are then conducted to the reactor vessel containing cyclones (not shown) where cracked products are separated from coked catalyst particles.

[0024] The LCN:cycle oil ratio at injection should range from 0.1 to 0.75, based on the combined weight of cycle oil and LCN. Preferably the ratio ranges from about 0.1 to about 0.6, and more preferably from about 0.2 to about 0.5.

10 [0025] The invention will now be further understood by reference to the following examples.

EXAMPLES

[0026] Comparative recycle options for short contact time FCC units were evaluated using a process model based on an existing FCC unit. Accordingly, the calculation directly compared existing unit performance with calculated results reflecting LCN and cycle oil injection in admixture with the heavy feed and approximately two meters upstream of the primary feed injectors. A cat cycle oil ("CCO") with boiling range of 240/370°C, light cat naphtha (LCN) with 10/100°C boiling range, a constant fresh feed rate of 172 m³/hr, and nominal recycle rate of 10 m³/hr were used in this example. The heavy feed employed contained VGO and about 4 wt.% vacuum resid.

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[0027] Feed properties are summarized in Table I.

TABLE I: FEEDSTOCK PROPERTIES

	VGO	VAC RESID
Gravity, API	23.8	11.4
Sulfur, wt.%	1.10	1.40
Thiophenic sulfur, wt.%	0.88	1.12
Nitrogen, wppm	1369	4111
Basic nitrogen, wppm	413	1247
Conradson carbon, wt.%	N.A.	15.3

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[0028] Catalyst properties are set forth in Table II:

TABLE II: CATALYST PROPERTIES

Unit Cell, $\oplus$	24.27
Surface area, m ² /gm	0.80
ABD, gm/cc	0.40
Pore Vol., cc/gm	1.52
REO, wt.%	1930
V, wppm	4150
Ni, wppm	61

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[0029] When recycle was employed, air blower rate ranged about 4% above the base case. Maximum catalyst circulation rate was 19 tons/min. Table III summarizes simulation results for neat LCN, neat CCO, and several examples of their blends.

TABLE III

CASE #	1 BASE	2 LCN RECYCLE	3 CCO RECYCLE	4 LCN & CCO RECYCLE	5 LCN & CCO RECYCLE	6 LCN & CCO RECYCLE	7 LCN & CCO RECYCLE
FRESH FEED RATE, T/HR	157.1	157.1	157.1	157.1	157.1	157.1	157.1
TOTAL FEED RATE, T/HR	157.1	164.2	166.2	164.8	164.5	164.3	164
FEED TEMP, DEG C	270	270	270	270	270	269	269
REACTOR TEMP, DEG C	525	525	525	525	525	525	525
REGEN TEMP, DEG C	706	698	702	700	700	699	699
CAT CIRC, T/M	17.27	18.86	18.47	18.6	18.6	18.7	18.8
CAT/OIL WT/WT (TOTAL FD)	6.6	6.89	6.67	6.76	6.8	6.84	6.86
TOTAL AIR, KNM3/HR	84.63	87.91	88.48	87.97	87.97	87.97	87.97
LCN RECYCLE, T/HR	0	7.1	0	2.3	3.5	4.6	5.2
CCO RECYCLE, T/HR	0	0	9.1	5.4	3.9	2.6	1.8
PRE-INJ VAP RES TIME, SEC	N/A	0.35	0.4	0.39	0.38	0.37	0.37
PRE-INJ TEMP, DEG C	N/A	691	698	695	694	693	693
430 F CONVERSION, WT%	72	70	71.87	71.24	70.96	70.67	70.5
02 - DRY GAS	3.63	4.49	3.94	4.1	4.2	4.29	4.34
PROPYLENE, WT% FF	3.94	4.38	4.08	4.18	4.23	4.28	4.3
PROPANE, WT% FF	1.28	1.43	1.41	1.42	1.42	1.43	1.43
BUTYLENES, WT% FF	5.41	6.06	5.67	5.8	5.87	5.94	5.96
BUTANES, WT% FF	2.83	2.93	2.89	2.9	2.91	2.92	2.92
LCN (C5/100 C) WT% FF	25.04	20.02	24.35	22.96	22.22	21.52	21.17
CCO (240/370 C) WT% FF	16.39	17.25	14.93	15.77	16.13	16.49	16.7
BTMS (370 c+), WT% FF	9.37	10.55	10.82	10.69	10.64	10.59	10.56
COKE, WT% FF	4.83	4.98	5.02	4.99	4.99	4.99	4.99

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[0030] Feed pre-heat and riser outlet temperatures are constant for each example. At approximately constant total recycle rate, the highest light olefin yields and the highest olefin to dry gas selectivity are achieved with LCN and CCO recycle. Cases with recycle of LCN and CCO streams in admixture with base gas oil feed results in improvements that are much less pronounced. Dry gas yields increase with increasing LCN recycle. There is a 2 wt.% 430°F conversion penalty for the neat LCN recycle case (and large LCN volume reduction), whereas the neat CCO recycle option gives a minimal conversion debit. In essence, examples 2 and 3 bracket the ideal situation wherein light olefins yields are increased without a large dry gas penalty and conversion of fresh feed is maximized.

[0031] Figure 2 shows that the ratio of light olefin yield increase to dry gas yield increase may be adjusted by including cycle oil with LCN recycle, in accord with the invention. The ordinate in Figure 2 shows the increase in light olefin yield divided by the increase in dry gas yield plotted for various LCN:cycle oil ratios on the abscissa. For the blend of LCN and CCO, the preferred blend composition contains about 30 wt.% LCN.

[0032] The calculated pre-injection vapor residence time for all examples is approximately constant at only 0.35-0.4 second. Extremely high (120-160) cat/oil ratios are realized at these elevated temperatures, and both catalytic and thermal reactions occur. While not wishing to be bound by any theory, it is believed that CCO injected into the upstream zone may provide an in situ quench for LCN cracking at this extraordinary intensity.

[0033] It should be noted that 430°F conversion decreases resulting from catalyst "pre-coking" prior to base feed injection. However, the conversion decrease is smaller for CCO compared to LCN at virtually identical coke yield. While not wishing to be bound, it is believed that recycling CCO drives bottoms yield up slightly more than recycling LCN at the same volumetric flow rate, but cycle oil conversion is enhanced.

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WHAT IS CLAIMED IS:

1. A fluid catalytic cracking process to increase yields of C₃ and C₄ olefins which comprises:

(a) conducting hot regenerated catalyst to an FCC unit having at least one riser reactor containing a downstream and an upstream reaction zone,

(b) contacting hot catalyst with a cycle oil, a light cat naphtha, and steam in the upstream reaction zone at a temperature of from about 620 to 775°C and a vapor residence time of cycle oil, naphtha, and steam of less than 1.5 sec. wherein at least a portion of the C₅ to C₉ olefins present in the light cat naphtha is cracked to C₃ and C₄ olefins, and wherein at least a portion of the saturates in the cycle oil is converted to lower boiling point products including C₃ and C₄ olefins,

(c) contacting at least the catalyst products of cycle oil and naphtha cracking, and steam from the upstream reaction zone with a heavy feedstock in the downstream reaction zone at an initial temperature of from about 600 to 750°C with vapor residence times of less than about 20 seconds,

(d) conducting spent catalyst, cracked products and steam from the first and second reaction zones to a separation zone,

(e) separating from the cracked products a cycle oil fraction, a light cat naphtha fraction, and steam from spent catalyst and recycling at least a portion of the cycle oil fraction and light cat naphtha fraction to the upstream reaction zone in step (b),

(f) conducting spent catalyst to a stripping zone and stripping spent catalyst under stripping conditions, and

(g) conducting stripped spent catalyst to a regeneration zone and regenerating spent catalyst under regeneration conditions.

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2. The process of claim 1 wherein the amount of steam in the upstream reaction zone is from 2 to 50 wt.%, based on total weight of light cat naphtha and cycle oil.

3. The process of claim 1 wherein the residence time of cycle oil, naphtha, and steam in the upstream reaction zone is less than about 1 sec.

4. The process of claim 1 wherein process conditions in step (b) include catalyst/oil ratios of 75 - 150 (wt/wt) at pressures of 100 - 400 kPa.

5. The process of claim 1 wherein process conditions in step (c) include catalyst/oil ratios of 4 - 10 at pressures of 100 - 400 kPa and vapor residence times of 2 - 20 sec.

6. The process of claim 1 wherein the feedstock in step (c) includes from 1 to 15 wt.%, based on feedstock, of a higher boiling fraction with initial boiling point greater than 565°C.