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NAPHTHA AND CYCLE OIL CONVERSION PROCESS**BACKGROUND**

[0001] The present invention relates to a process for converting naphthas and cycle oils produced in catalytic cracking reactions into light olefins. In one embodiment, the invention relates to a process for converting a light catalytically cracked naphtha ("light cat naphtha" or "LCN") and light catalytically cracked cycle oil ("light cat cycle oil," "LCO," or "LCCO") into light olefins using a conventional zeolite catalytic cracking catalyst.

[0002] Cycle oils such as LCCO produced in fluidized catalytic cracking ("FCC") reactions contain multi-ring aromatic species such as naphthalene. The need for blendstocks for forming low emissions fuels has created an increased demand for FCC products that contain a diminished concentration of multi-ring aromatics. There is also an increased demand for FCC products containing increased concentrations of light olefins that may be separated for use in alkylation, oligomerization, polymerization, and MTBE and ETBE synthesis processes. There is a particular need for low-emissions, high-octane FCC products having an increased concentration of C₂-C₄ olefins and a reduced concentration of multi-ring aromatics and olefins of higher molecular weight.

[0003] A high-octane gasoline may be conventionally produced by hydroprocessing a LCO and then re-cracking the hydroprocessed cycle oil in the FCC unit or in an additional catalytic cracking unit, sometimes referred to as an outboard cracker.

[0004] In such conventional processes, hydroprocessing a cycle oil, such as LCCO, results in partial saturation of bicyclic aromatic hydrocarbon and carbonaceous species, such as naphthalene, to produce tetrahydronaphthalene

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and alkyl-substituted derivatives thereof ("tetrahydronaphthalenes"). The hydroprocessing is performed under conditions that result in partially saturated aromatic species in the cycle oil. In one conventional process, a cycle oil containing naphthalene as the most abundant aromatic species is hydroprocessed under relatively mild conditions so that tetrahydronaphthalenes (and not decahydronaphthalenes) are the most abundant aromatic species in the hydroprocessed product.

[0005] Unfortunately, re-cracking a hydroprocessed cycle oil containing primarily partially-saturated species in the presence of a naphtha boiling range stream such as LCN results in undesirable hydrogen transfer reactions that convert partially saturated species, such as tetrahydronaphthalenes, to polynuclear aromatics such as naphthalene. The result is a decrease in the amount of olefins produced in the re-cracking step.

[0006] There remains a need, therefore, for processes for forming light olefins (C_2 - C_5) from naphtha and hydroprocessed cycle oils, such as LCCO, that increase the olefin concentration in the resulting product.

SUMMARY OF THE INVENTION

[0007] One embodiment of the invention comprises a process for catalytically cracking a hydrocarbonaceous feed. The process comprises the steps of: (a) introducing a regenerated catalyst into a FCC riser reactor having a first reaction zone and a second reaction zone, wherein the first reaction zone is downstream from the second reaction zone; (b) introducing the hydrocarbonaceous feed into the first reaction zone; (c) contacting the hydrocarbonaceous feed with a catalytically effective amount of the catalyst in the first reaction zone under hydrocarbonaceous feed catalytic cracking conditions to form a cracked product; (d) separating the cracked product from

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the catalyst; (e) stripping the catalyst; (f) separating at least a naphtha fraction and a cycle oil containing aromatic species from the cracked product; (g) converting a substantial portion of the aromatic species in the cycle oil to decahydronaphthalenes, thereby forming a hydroprocessed cycle oil; (h) contacting the catalyst from step (e) with a gas comprising at least oxygen to form a regenerated catalyst; (i) introducing the naphtha fraction and the hydroprocessed cycle oil into the second reaction zone; and, (j) contacting the regenerated catalyst with the naphtha fraction and the hydroprocessed cycle oil under cycle oil catalytic cracking conditions.

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[0008] Another embodiment of the invention comprises a process for catalytically cracking a hydrocarbonaceous feed. The process comprises the steps of: (a) contacting the hydrocarbonaceous feed with a catalytic cracking catalyst in a FCC reactor under catalytic cracking conditions to form a cracked product; (b) separating at least a naphtha fraction and a cycle oil containing aromatic species from the cracked product; (c) converting a substantial portion of the aromatic species in the cycle oil to decahydronaphthalenes, thereby forming a hydroprocessed cycle oil; and, (d) introducing the naphtha fraction and the hydroprocessed cycle oil into the FCC reactor at a point upstream from a point at which the hydrocarbonaceous feed is contacted with the catalytic cracking catalyst.

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DETAILED DESCRIPTION OF THE INVENTION

[0009] The invention is based on the discovery that recycling a naphtha and a hydroprocessed cycle oil containing a significant amount of decahydronaphthalenes to an FCC reaction zone along the primary feed riser at a point upstream of gas oil or residual oil feed injection results in beneficial conversion of the naphtha and the hydroprocessed cycle oil into light olefins, such as propylene. Applicants believe that injecting such recycle streams into

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the FCC reaction zone at a point upstream of gas oil or residual oil injection suppresses undesirable hydrogen transfer reactions by re-cracking potential hydrogen donors present in the cycle oil before such donors can contact the primary hydrocarbonaceous feed .

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[0010] While not wishing to be bound by any theory, applicants believe that the substantial concentration of propylene in the cracked product results from the naphtha and the hydroprocessed cycle oil cracking in the second reaction zone. Applicants also believe that saturating aromatic polycyclic species, such as naphthalene and alkyl substituted derivatives thereof (‘‘naphthalenes’’) and tetrahydronaphthalenes in the cycle oil diminishes detrimental hydrogen transfer reactions between the hydroprocessed cycle oil and hydrogen receptor species in the naphtha. Consequently, the formation of undesirable polynuclear aromatic compounds is avoided, allowing at least a portion of the saturated polycyclic species to crack to light olefins, such as propylene.

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[0011] As used herein, cycle oil includes 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). Naphtha refers to a hydrocarbon stream having a final boiling point at atmospheric pressure less than about 190°C and may be derived from sources such as pipe stills (straight run naphtha) and catalytic cracking units (cat naphtha). Light cat naphtha has a final boiling point less than about 150°C (300°F) and contains olefins in the C₅-C₉ range, single ring aromatics (C₆-C₉) and paraffins in the C₅-C₉ range. Preferably, hydroprocessed cycle oil and light cat naphtha (also referred to herein as the naphtha fraction) are injected into

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the second reactor zone together with 2 to 50 wt.% of steam based on the combined total weight of hydroprocessed cycle oil and naphtha fraction.

[0012] Hydrocarbonaceous feeds to the first reaction zone of the catalytic cracking process described herein include naphtha, hydrocarbon oils boiling in the range of about 430°F to about 1050°F (220-565°C), such as gas oil; heavy hydrocarbonaceous oils comprising materials boiling above 1050°F (565°C), heavy and reduced petroleum crude oil; petroleum atmospheric distillation bottoms; petroleum vacuum distillation bottoms; pitch, asphalt, bitumen, other heavy hydrocarbon residues; tar sand oils; shale oil; liquid products derived from coal liquefaction processes, and mixtures thereof. The hydrocarbonaceous feeds may or may not contain amounts of sulfur, nitrogen and other constituents normally found in petroleum feedstocks.

[0013] The cracking process may be performed in one or more conventional FCC process units. Each unit comprises a riser reactor having a first reaction zone and a second reaction zone upstream of the first reaction zone, a stripping zone, a catalyst regeneration zone, and at least one separation zone to separate the different products. The units may also comprise solid-gas separation zones that may comprise one or more cyclones to separate the catalyst from the vapor products.

[0014] The feed passes to the riser reactor where it is injected into the first reaction zone wherein the primary feed contacts a flowing source of hot, regenerated catalyst. The hot catalyst vaporizes and cracks the primary feed at a temperature from about 450°C to 650°C, preferably from about 525°C to 600°C. The cracking reaction deposits carbonaceous material, also referred to as coke, on the catalyst, thereby deactivating the catalyst. The cracked products may be separated from the coked catalyst and at least a portion of the cracked products

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may be passed to a separator, such as a fractionator. The fractionator separates at least a naphtha fraction and a cycle oil fraction from the cracked products.

[0015] The coked catalyst flows through the stripping zone where a stripping agent, such as steam, strips the volatiles (strippable hydrocarbons) from the catalyst particles. The stripping may be performed under low severity conditions in order to retain adsorbed hydrocarbons for heat balance. The stripped catalyst is then passed to the regeneration zone where it is regenerated by burning coke on the catalyst in the presence of an oxygen-containing gas, preferably air. Decoking restores catalyst activity and simultaneously heats the catalyst to, e.g., 650°C to 800°C. The hot catalyst is then recycled to the FCC riser reactor at a point near or just upstream from the second reaction zone. Flue gas formed by burning coke in the regenerator may be treated for removal of particulates and for conversion of carbon monoxide.

[0016] As discussed, at least a naphtha fraction and a cycle oil fraction are separated from the cracked products. Subsequently, at least a portion of the cycle oil is hydroprocessed in the presence of a hydroprocessing catalyst under hydroprocessing conditions in order to form a hydroprocessed cycle oil having a substantial concentration of decahydronaphthalene and alkyl-substituted derivatives thereof (decahydronaphthalenes). The hydroprocessing may occur in one or more hydroprocessing reactors. At least a portion of the hydroprocessed cycle oil passes to the riser reactor and injected with the naphtha fraction into the second reaction zone.

[0017] Cycle oil hydroprocessing is passed under conditions that convert aromatic species such as naphthalene and alkyl-substituted derivatives thereof (naphthalenes) and tetrahydronaphthalene and alkyl-substituted derivatives thereof (tetrahydronaphthalenes) to decahydronaphthalenes. While not wishing

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to be bound by any theory or model, applicants believe that the hydroprocessing conditions result in a hydroprocessed cycle oil that has a greater propensity for cracking to light olefins (C_2 - C_6) than cycle oils hydroprocessed in accordance with the conventional processes that aim to produce significant amounts of
5 tetrahydronaphthalenes.

[0018] Preferably, the hydroprocessing is conducted so that decahydronaphthalenes and derivatives thereof are the most abundant 2-ring species in the hydroprocessed cycle oil. More preferably,
10 decahydronaphthalenes and derivatives thereof are the most abundant saturated species in the hydroprocessed cycle oil.

[0019] Preferably, the total aromatic species content in the hydroprocessed cycle oil ranges from about 0 to about 5 wt.%, with a total 2-ring
15 or larger aromatic species content ranges from about 0 to about 1 wt.%, preferably 0-0.1 wt.%, more preferably 0-0.05 wt.%, most preferably 0-0.01 wt.% based upon the total weight of the hydroprocessed cycle oil. Still more preferably, the total aromatic species content in the hydroprocessed cycle oil ranges is less than 5 wt. %, more preferably less than about 1 wt.%, more
20 preferably from about 0 to about 0.6 wt.%, with a total 2-ring or larger aromatic species content less than 1 wt.%, more preferably less than 0.1 wt.%, more preferably less than or equal to about 0.01 wt.% based upon the total weight of the hydroprocessed cycle oil.

25 [0020] The first reaction zone process conditions include temperatures from about 450°C to about 650°C, preferably from about 525°C to 600°C, hydrocarbon partial pressures from about 10 to 40 psia, preferably from about 20 to 35 psia; and a catalyst to heavy feed (wt./wt.) ratio of about 3 to 12, preferably about 4 to 10, where the catalyst weight is the total weight of the catalyst

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composite. Though not required, steam may be concurrently introduced with the primary feed into the first reaction zone. The steam may comprise up to about 10 wt.%, preferably about 1 to about 2 wt.%, of the total weight of the primary feed. Preferably, the primary feed residence time in the first reaction zone is less than about 10 seconds, more preferably between about 1 and 10 seconds.

[0021] The second reaction zone process conditions include temperatures from about 550°C to about 700°C, preferably from about 525°C to 650°C, hydrocarbon partial pressures from about 10 to 40 psia, preferably from about 20 to 35 psia; and a catalyst to hydrocarbon (cycle oil and naphtha) weight-to-weight ratio of about 5 to 100, preferably about 10 to 100, where the catalyst weight is the total weight of the catalyst composite. Though not required, steam may be concurrently introduced with the naphtha and hydroprocessed cycle oil feed into the second reaction zone. The steam may comprise from about 2 wt.% to about 50 wt.%, preferably up to about 10 wt.%, based on the weight of the naphtha and cycle oil. The naphtha fraction-hydroprocessed cycle oil residence time in the second reaction zone is preferably less than about 10 seconds, more preferably between about 0.1 to about 10 seconds.

[0022] The catalyst can be any catalyst typically used to catalytically crack hydrocarbonaceous feed s. Preferably, the catalytic cracking catalyst comprises a crystalline tetrahedral framework oxide component. This component is used to catalyze 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 silicoaluminophosphates (SAPOs). More preferably, the crystalline framework oxide component is a zeolite. The catalyst may comprise one or more individual

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catalyst particles and other reactive and non-reactive components. More than one type of catalyst particle may be present in the catalyst. For example, individual catalyst particles may contain large-pore zeolite, shape-selective zeolite, and mixtures thereof.

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[0023] One catalyst particle useful in the invention contains at least one crystalline aluminosilicate, also referred to as zeolite, having an average pore diameter greater than about 0.7 nanometers (nm), also referred to herein as a large-pore zeolite cracking catalyst. The pore diameter also sometimes referred to as effective pore diameter may be measured using standard adsorption techniques and hydrocarbons of known minimum kinetic diameters. See Breck, *Zeolite Molecular Sieves*, 1974 and Anderson et al., *J. Catalysis* 58, 114 (1979), both of which are incorporated herein by reference. Zeolites useful in the invention are described in the "Atlas of Zeolite Structure Types," eds. W. H. Meier and D. H. Olson, Butterworth-Heinemann, Third Edition, 1992, which is hereby incorporated by reference. As discussed, the catalyst may be in the form of particles containing zeolite. The catalyst may also include fines, inert particles, particles containing a metallic species, and mixtures thereof. Particles containing metallic species include platinum compounds, platinum metal, and mixtures thereof.

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[0024] Catalyst particles may contain metals such as platinum, promoter species such as phosphorous-containing species, clay filler, and species for imparting catalytic functionality such as bottoms cracking and metals passivation and can be provided by incorporating aluminum-containing species.

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[0025] Suitable zeolite in such catalyst particles include zeolites which are iso-structural to zeolite Y. These include the ion-exchanged forms such as the rare-earth hydrogen and ultra stable (USY) form. The zeolite may range in size

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from about 0.1 to about 10 microns, preferably from about 0.3 to about 3 microns. The zeolite will be mixed with a suitable porous matrix material in order to form the fluid catalytic cracking catalyst. Non-limiting porous matrix materials which may be used in the practice of the present invention include alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, as well as ternary compositions, such as silica-alumina-thoria, silica-alumina-zirconia, magnesia and silica-magnesia-zirconia. The matrix may also be in the form of a cogel. The matrix itself may possess catalytic properties, generally of an acidic nature.

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[0026] Another cracking catalyst contains a mixture of zeolite Y and zeolite beta. The Y and beta zeolite may be on the same catalyst particle, on different particles, or some combination thereof. Such catalysts are described in U.S. Patent No. 5,314,612, incorporated by reference herein. Such catalyst particles consist of a combination of zeolite Y and zeolite beta combined in a matrix comprised of silica, silica-alumina, alumina, or any other suitable matrix material for such catalyst particles. The zeolite portion of the resulting composite catalyst particle will consist of about 25 to about 95 wt.% zeolite Y with the balance comprising zeolite beta.

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[0027] Yet another cracking catalyst contains a mixture of zeolite Y and a shape selective zeolite species such as ZSM-5 or a mixture of an amorphous acidic material and ZSM-5. The Y zeolite (or alternatively the amorphous acidic material) and shape selective zeolite may be on the same catalyst particle, on different particles, or some combination thereof. Such catalysts are described in U.S. Patent No. 5,318,692, incorporated by reference herein. The zeolite portion of the catalyst particle will typically contain from about 5 wt.% to about 95 wt.% zeolite-Y (or alternatively the amorphous acidic material) and the balance of the zeolite portion being ZSM-5.

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[0028] Shape-selective zeolite species include medium-pore-size zeolites generally having a pore size from about 0.5 nm, to about 0.7 nm, and including MFI, MFS, MEL, MTW, EUO, MTT, HEU, FER, and TON structure-type
5 zeolites (IUPAC Commission of Zeolite Nomenclature). Non-limiting examples of such medium pore size zeolites, include ZSM-5, ZSM-12, ZSM-22, ZSM-23, ZSM-34, ZSM-35, ZSM-38, ZSM-48, ZSM-50, silicalite, and silicalite 2. The most preferred is ZSM-5, which is described in U.S. Patent Nos. 3,702,886 and 3,770,614. ZSM-11 is described in U.S. Patent No. 3,709,979; ZSM-12 in U.S.
10 Patent No. 3,832,449; ZSM-21 and ZSM-38 in U.S. Patent No. 3,948,758; ZSM-23 in U.S. Patent No. 4,076,842; and ZSM-35 in U.S. Patent No. 4,016,245. All of the above patents are incorporated herein by reference.

[0029] Other suitable medium-pore-size zeolites include the
15 silicoaluminophosphates (SAPO), such as SAPO-4 and SAPO-11 which is described in U.S. Patent No. 4,440,871; chromosilicates; gallium silicates; iron silicates; aluminum phosphates (ALPO), such as ALPO-11 described in U.S. Patent No. 4,310,440; titanium aluminosilicates (TASO), such as TASO-45 described in EP-A No. 229,295; boron silicates, described in U.S. Patent No.
20 4,254,297; titanium aluminophosphates (TAPO), such as TAPO-11 described in U.S. Patent No. 4,500,651; and iron aluminosilicates.

[0030] The large-pore and shape-selective zeolites in the catalytic species can include "crystalline admixtures" which are thought to be the result of faults
25 occurring within the crystal or crystalline area during the synthesis of the zeolites. Examples of crystalline admixtures of ZSM-5 and ZSM-11 are disclosed in U.S. Patent No. 4,229,424 which is incorporated herein by reference. The crystalline admixtures are themselves medium pore, i.e., shape selective, size zeolites and are not to be confused with physical admixtures of

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zeolites in which distinct crystals of crystallites of different zeolites are physically present in the same catalyst composite or hydrothermal reaction mixtures.

5 **[0031]** As discussed, the present process comprises cracking a primary feed in the first reaction zone of a FCC riser reactor in order to form a cracked product. At least a portion of the naphtha and cycle oil are separated from the cracked product, and the cycle oil fraction is hydroprocessed to form a hydroprocessed cycle oil having a significant decahydronaphthalenes
10 concentration. The hydroprocessed cycle oil and naphtha fraction pass to the riser reactor for injection into the second reaction zone. The cycle oil hydroprocessing may occur in a hydroprocessing reactor under hydroprocessing conditions in the presence of a hydroprocessing catalyst.

15 **[0032]** Preferably, the naphtha fraction: hydroprocessed cycle oil ratio for injection into the second reaction zone should range from about 0 to about 0.75, based on the combined weight of cycle oil and naphtha fraction. Preferably the ratio ranges from about 0.1 to about 0.75, and more preferably from about 0.2 to about 0.6.

20 **[0033]** The term hydroprocessing is used broadly herein, and includes for example hydrogenation or saturation of aromatic species, hydrotreating, hydrofining, and hydrocracking. As is known by those of skill in the art, the degree of hydroprocessing can be controlled through proper selection of catalyst
25 and by optimizing operation conditions. Preferably, the hydroprocessing converts a significant amount of aromatic species, such as naphthalene and tetrahydronaphthalene and derivatives thereof, to decahydronaphthalene and derivatives thereof using a catalytically effective amount of a hydrogenation

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catalyst and hydrogen. Objectionable species can also be removed by the hydroprocessing reactions.

[0034] Hydroprocessing may be performed in one or more stages consistent with the objective of maximizing conversion of multi-ring aromatics species (e.g., naphthalenes) to the corresponding fully saturated species (e.g., decahydronaphthalene). For a single-stage operation, the reaction is performed at a temperature ranging from about 200°C to about 550°C, more preferably from about 250°C to about 400°C. The reaction pressure preferably ranges from about 1000 to about 3000 psig, more preferably from about 1200 to about 2500 psig, and still more preferably from about 1300 to about 2000 psig. The space velocity ranges from about 0.1 to 6 V/V/hr, preferably from about 0.5 to about 2 V/V/hr, more preferably from about 0.8 to about 2 V/V/hr. V/V/hr is the volume of oil feed per hour per volume of catalyst.

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[0035] The hydrogen-containing gas is added to establish a hydrogen charge rate ranging from about 1,000 to about 15,000 standard cubic feet per barrel (SCF/B), more preferably from about 5,000 to about 10,000 SCF/B. Actual conditions employed will depend on factors such as feed quality and catalyst but should be consistent with the objective of maximizing conversion of multi-ring aromatic species to decahydronaphthalenes.

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[0036] In a two-stage operation, the cycle oil is first hydroprocessed in a first stage to remove substantial amounts of sulfur and nitrogen, and convert bicyclic aromatics, such as naphthalenes, to partially saturated species such as tetrahydronaphthalenes, more preferably to completely saturated species, such as decahydronaphthalenes. The second-stage hydroprocessing is primarily a hydrogenation reaction performed at a temperature ranging from about 100°C to about 600°C, preferably from about 100°C to about 450°C, more preferably

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from about 200°C to about 400°C. The reaction pressure ranges from about 100 to about 3000 psig, preferably from about 450 to about 2000 psig, more preferably from about 1300 psig to about 2000 psig. The space velocity preferably ranges from about 0.1 to 6 V/V/hr, preferably about 0.8 to about 2 V/V/hr.

[0037] The hydrogen-containing gas is added to establish a hydrogen charge rate ranging from about 500 to about 15,000 standard cubic feet per barrel (SCF/B), more preferably from about 500 to about 10,000 SCF/B. Actual conditions employed will depend on factors such as feed quality and catalyst but should be consistent with the objective of maximizing the concentration of decahydronaphthalenes in the hydroprocessed cycle oil introduced into the second FCC reactor.

[0038] Hydroprocessing conditions can be maintained using any of several types of hydroprocessing reactors. Trickle bed reactors are most commonly employed in petroleum refining applications with co-current downflow of liquid and gas phases over a fixed bed of catalyst particles. It can be advantageous to utilize alternative reactor technologies. In countercurrent-flow reactors, the liquid phase passes down through a fixed bed of catalyst against upward-moving treat gas. Countercurrent-flow reactors obtain higher reaction rates and alleviate aromatic hydrogenation equilibrium limitations inherent in co-current flow trickle bed reactors.

[0039] Moving bed reactors are employed to increase metal and particulate tolerance in the hydroprocessor feed stream. Moving bed reactor types generally include reactors wherein a captive bed of catalyst particles is contacted by upward-flowing liquid and treat gas. The catalyst bed may be slightly expanded by the upward flow or substantially expanded or fluidized by

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increasing flow rate via liquid recirculation (expanded bed or ebullating bed), using smaller size catalyst particles that are more easily fluidized (slurry bed), or both. Moving bed reactors utilizing downward-flowing liquid and gas may also be used because they would enable on-stream catalyst replacement. In any case, catalyst can be removed from a moving bed reactor during onstream operation, enabling economic application when high levels of metals in the hydroprocessor feed would otherwise cause short run lengths in the alternative fixed bed designs.

10 **[0040]** Expanded or slurry bed reactors with upward-flowing liquid and gas phases enable economic operation with hydroprocessor feedstocks containing significant levels of particulate solids, by permitting long run lengths without risking shutdown from fouling. Such a reactor is especially beneficial in cases where the hydroprocessor feedstocks include solids greater than about 25
15 microns and where the hydroprocessor feedstocks contain contaminants that increase the propensity for accumulating foulants such as olefinic, diolefinic, or oxygenated species.

20 **[0041]** The catalyst used in the hydroprocessing stages can be any hydroprocessing catalyst(s) suitable for aromatic saturation, desulfurization, denitrogenation or any combination thereof. Suitable catalysts used to completely hydrogenate the cycle oil include monofunctional and bifunctional, monometallic and multimetallic noble metal-containing catalysts. Preferably, the catalyst comprises at least one Group VIII metal and a Group VI metal on an
25 inorganic refractory support. Any suitable inorganic oxide support material may be used for the hydroprocessing catalyst of the present invention. Preferred are alumina and silica-alumina, including crystalline alumino-silicate such as zeolite. The silica content of the silica-alumina support can be from 2-30 wt.%, preferably 3-20 wt.%, more preferably 5-19 wt.%. Other refractory inorganic

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compounds may also be used, non-limiting examples of which include zirconia, titania, magnesia, and the like. The alumina can be any of the aluminas conventionally used for hydroprocessing catalysts. Such aluminas are generally porous amorphous alumina having an average pore size from 50-200 Å, preferably 70-150 Å, and a surface area from 50-450 m²/g.

[0042] The Group VIII and Group VI compounds are well known to those of ordinary skill in the art and are well defined in the Periodic Table of the Elements. The Group VIII metal may be present in an amount ranging from 2-20 wt.%, preferably 4-12 wt.% and may include Co, Ni, and Fe. The Group VI metals may be W, Mo, or Cr, with Mo preferred. The Group VI metal may be present in an amount ranging from 5-50 wt.%, preferably from 20-30 wt.%. The hydroprocessing catalyst preferably includes a Group VIII noble metal present in an amount ranging from 0-10 wt.%, preferably 0.3-3.0 wt.%. The Group VIII noble metal may include, but is not limited to, Pt, Ir, or Pd, preferably Pt or Pd, to which is generally attributed the hydrogenation function.

[0043] One or more promoter metals selected from metals of Groups IIIA, IVA, IB, VIB, and VIIB of the Periodic Table of the Elements may also be present. The promoter metal, can be present in the form of an oxide, sulfide, or in the elemental state. It is also preferred that the catalyst compositions have a relatively high surface area, for example, about 100 to 250 m²/g. The Periodic Table of which all the Groups herein refer to can be found on the last page of Advanced Inorganic Chemistry, 2nd Edition, 1966, Interscience publishers, by Cotton and Wilkinson. All metals weight percents for the hydroprocessing catalyst are given on support. The term "on support" means that the percents are based on the weight of the support. For example, if a support weighs 100 g, then 20 wt.% Group VIII metal means that 20 g of the Group VIII metal is on the support.

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[0044] After hydroprocessing, the hydroprocessed cycle oil is passed to the riser reactor for injection with the naphtha fraction into the second reaction zone wherein the cycle oil is cracked into lower molecular weight cracked products and undesirable hydrogen transfer reactions are suppressed. In addition to cycle oil, cracked products formed in the riser reactor include naphtha in amounts ranging from about 5 wt.% to about 50 wt.%, butanes in amounts ranging from about 2 wt.% to about 15 wt.%, butenes in amounts ranging from about 4 wt.% to about 11 wt.%, propane in amounts ranging from about 0.5 wt.% to about 3.5 wt.%, and propylene in amounts ranging from about 5 wt.% to about 20 wt.%. All wt.% are based on the total weight of the cracked product. Preferably, at least 90 wt.% of the cracked products have boiling points less than 220°C.

[0045] This invention is illustrated by, but not limited to, the following examples that are for illustrative purposes only.

EXAMPLES

Example 1

[0046] A calculated comparison of cycle oil injection for re-cracking in a FCC reaction zone is set forth in Table 1. Simulations 1, 2, 3, and 4 are compared to a base case FCC process with no cycle oil recycle. In case 1, heavy cycle oil is separated from the FCC products and recycled to the FCC process via injection with the primary feed. In case 2, recycled heavy cycle oil is injected upstream of main feed injection. In case 3, the heavy cycle oil is injected upstream of main feed injection as in case 2, and the heavy cycle oil is hydrogenated to produce a significant amount of tetrahydronaphthalenes (Table 2, column 1) prior to upstream injection. Accordingly, the hydrogenation of case 3 results in little, if any, conversion of aromatic species to

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decahydronaphthalenes. In case 4, the heavy cycle oil is hydroprocessed under conditions sufficient to convert a significant amount of the cycle oil's aromatic species to decahydronaphthalenes (Table 2, column 2). In all cases, a conventional large-pore zeolite catalytic cracking catalyst was present in the reaction zone. No shape-selective zeolite was employed. The table shows that some advantageous increase in propylene yield occurs when the heavy cycle oil is injected with the primary feed (base case and case 1). Case 2 illustrates further increase in propylene yield when, in accordance with this invention, the heavy cycle oil is injected to a second reaction zone upstream from the first injection zone. Cases 3 and 4 show that additional propylene yield may be obtained via heavy cycle oil hydroprocessing prior to injection.

[0047] Moreover, direct comparison of cases 3 and 4 shows that hydroprocessing under conditions that produce significant conversion to decahydronaphthalenes results in greater propylene yield with increased loss in naphtha yield, less coke make, and a nearly 100% increase in heavy cycle oil conversion. While not wishing to be bound by any theory, it is believed that the large increase in heavy cycle oil conversion to decahydronaphthalenes in case 4 results in a suppression of undesirable hydrogen transfer reactions present in case 3. These undesirable hydrogen transfer reactions convert partially saturated species, such as tetrahydronaphthalenes, into naphthalenes in the FCC second reaction zone.

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Table 1

CASE	BASE	1	2	3	4
HCO Recycle, vol%	0	8.8	8.8	8.8	8.8
Injection Location		Main Feed	Pre- Injection	Pre- Injection	Pre- Injection
Yields, Wt.% FF					
C ₂ - Dry Gas	2.93	2.99	3.18	3.2	3.34
C ₃ =	3.94	3.99	4.09	4.09	4.33
C ₄ =	5.41	5.53	5.67	5.72	6.03
LPG	13.46	13.8	14.06	14.2	15.05
Naphtha	46.39	48.33	45.5	45.85	48.85
LCO	5.93	5.86	6.94	7.02	6.54
HCO	16.39	13.59	13.3	12.91	9.66
BTMS	9.37	9.32	11.18	11.08	10.94
Coke	4.83	5.41	5.11	5.07	4.9
430°F(220°C) Conv.	72	74.7	72.2	73.2	77.1
% HCO Converted	0	31	34	38	73

[0048] Simulated process conditions for this comparison include a riser outlet temperature of 977 °F (525°C) and a catalyst to total feed weight ratio of 6.6.

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Example 2

[0049] In accordance with another embodiment, this example describes hydroprocessing a cycle oil stream and then injecting it at a point in a FCC riser reactor upstream from the normal primary feed injectors. This provides a high temperature, high catalyst to oil ratio, short residence time region wherein the hydroprocessed cycle oil may be converted to naphtha and light olefins.

Catalytic cracking conditions in the second reaction zone include temperatures ranging from about 1000°F to about 1350°F (538°C - 732°C), catalyst to oil weight ratios of about 25-150, and vapor residence times of 0.1-1.0 seconds in the pre-injection zone (second reaction zone), as set forth in Table 3.

Conventional catalytic cracking conditions were used in the first reaction zone, with temperature ranging from about 950°F (510°C) to about 1050°F (565°C) and the catalyst to oil weight ratio between about 4 and about 10.

[0050] The cycle oils were hydrogenated to produce a significant amount of tetrahydronaphthalenes (Table 2, column 1) or under different hydrogenation conditions to produce significant amounts of decahydronaphthalenes (Table 2, column 2) prior to upstream injection into the FCC unit. As set forth in Table 2, the hydrogenation conditions to form decahydronaphthalenes result in nearly complete saturation of aromatic species present in the hydroprocessed cycle oil.

Table 2

	Hydrogenation to at least partially saturate aromatics (form Tetrahydronaphthalenes)	Hydrogenation to substantially saturate aromatics
Conditions		
Catalyst	NiMo/Al ₂ O ₃	Pt/Al ₂ O ₃
Temperature (°F)/(°C)	700 / 371	550 / 288
Pressure (psig)	1200	1800
LHSV	0.7	1.7
H ₂ Treat Gas Rate (SCF/B)	5500	5000
Product Properties		
Boiling Point Distribution		
0.5 wt.% (°F)/(°C)	224.6 / 107.0	219.7 / 104.3
50.0 wt.% (°F)/(°C)	513.4 / 267.4	475.5 / 246.4
99.5 wt.% (°F)/(°C)	720.4 / 382.4	725.4 / 385.2
Gravity (°API)	26.2	33.2
Total Aromatics (wt.%)	57.6	0.6
One-Ring Aromatics (wt.%)	43.1	0.6
Feedstock Properties		

	Hydrogenation to at least partially saturate aromatics (form Tetrahydronaphthalenes)	Hydrogenation to substantially saturate aromatics
Boiling Point Distribution		
0.5 wt. % (°F)/(°C)	299.8 / 148.8	224.6 / 107.0
50.0 wt. % (°F)/(°C)	564.9 / 296.1	513.4 / 267.4
99.5 wt. % (°F)/(°C)	727.8 / 386.6	720.4 / 382.4
Gravity (°API)	13.8	26.2
Total Aromatics (wt. %)	83.5	57.6
One-Ring Aromatics (wt. %)	9.7	43.1

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[0051] Cracking conditions for the pre-injected hydroprocessed cycle oil in the presence of catalytic cracking catalyst mixtures of large-pore zeolite catalyst in combination with shape-selective zeolite catalysts, such as ZSM-5 in a Microactivity Test Unit ("MAT") are set forth in Table 3.

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[0052] MAT tests and associated hardware are described in Oil and Gas Journal 64, 7, 84, 85, 1966, and Oil and Gas Journal, November 22, 1971, 60-68. Conditions used herein included temperatures 550°, 650°C, run time 0.5 sec., catalyst charge 4.0 g, feed volume 0.95-1.0 cm³, and catalyst to oil weight ratio of 4.0-4.2.

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[0053] Catalysts A and B are commercially available, conventional, large-pore FCC catalysts containing Y-zeolite, while catalyst C contains ZSM-5.

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[0054] As shown in Table 3, hydrogenation to form substantially saturate aromatics (resulting in a significant amount of decahydronaphthalenes) prior to pre-injection results in increased FCC conversion (column 2) compared to pre-injection of a cycle oil that was subjected to hydrogenation under different conditions that only partially saturated aromatics (to form a significant amount of tetrahydronaphthalenes) and then pre-injected and cracked under similar conditions (column 1). Moreover, further increases in propylene production can be obtained when a shape selective catalyst is combined with large pore FCC catalyst, as shown in column 3.

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Table 3

Feedstock	Hydroprocessed cycle oil with partially saturated aromatics (e.g., forming Tetrahydro-naphthalenes)	Hydroprocessed cycle oil with substantially saturated aromatics	Hydroprocessed cycle oil with substantially saturated aromatics
Catalyst (steamed)	100% Catalyst A	100% Catalyst A	90% Catalyst B 10% Catalyst C
Temp. (°F)/(°C)	1020 / 549	1020 / 549	1200 / 649
Cat Oil	3.96	4.15	3.98
Conversion	81.2	93.3	89.1
Yields (wt.%)			
C ₂ - Dry Gas	3.5	3.3	9.5
Propylene	5.4	7.1	13.3
Propane	1.9	2.3	0.9
Butenes	4.2	4.5	10.7
Butanes	8.8	13.2	3.0
Naphtha	53.2	59.8	48.4
430°F+ (220°C+)	18.8	6.7	10.9
Coke	4.3	3.1	3.3

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WHAT IS CLAIMED IS:

1. A process for catalytically cracking a hydrocarbonaceous feed comprising the steps of:

5 (a) introducing a catalytic cracking catalyst into a FCC riser reactor, said riser reactor having a first reaction zone and a second reaction zone, said first reaction zone downstream from said second reaction zone;

(b) introducing said hydrocarbonaceous feed into said first reaction zone;

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(c) contacting said hydrocarbonaceous feed with said catalytic cracking catalyst in said first reaction zone under catalytic cracking conditions to produce a cracked product;

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(d) separating said cracked product from said catalyst;

(e) stripping said catalyst;

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(f) separating at least a naphtha fraction and a cycle oil fraction from said cracked product, said cycle oil fraction containing aromatic species;

(g) hydroprocessing at least a portion of said cycle oil fraction to saturate a substantial portion of said aromatic species in said cycle oil fraction, thereby forming a hydroprocessed cycle oil;

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(h) contacting said catalyst from step (e) with a gas comprising oxygen;

(i) introducing said naphtha fraction and said hydroprocessed cycle oil into said second reaction zone; and,

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(j) contacting said naphtha fraction and said hydroprocessed cycle oil with said catalytic cracking catalyst under catalytic cracking conditions in said second reaction zone, thereby producing a product stream having an increased concentration of C₂ to C₄ olefins.

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2. The process according to claim 1 further comprising the step of introducing steam into said first reaction zone.

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3. The process according to claim 1 further comprising the step of introducing steam into said second reaction zone.

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4. The process according to claim 1 wherein said naphtha fraction and said hydroprocessed cycle oil are injected into said second reaction zone at a rate sufficient to keep the weight ratio of the total naphtha fraction and hydroprocessed cycle oil to said catalyst between about 1 and 100.

5. The process according to claim 1 wherein the temperature in said first reaction zone is between about 450°C and about 650°C.

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6. The process according to claim 1 wherein the temperature in said second reaction zone is between about 550°C and about 700°C.

7. The process according to claim 1 wherein the weight ratio of said naphtha fraction to hydroprocessed cycle oil is between about 1 and 10.

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8. The process according to claim 1 wherein the weight of said aromatic species in said hydroprocessed cycle oil is less than or equal to about 1 wt.% of the total weight of the hydroprocessed cycle oil introduced into said second reaction zone.

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9. A process for catalytically cracking a hydrocarbonaceous feed comprising the steps of:

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(a) contacting said hydrocarbonaceous feed with a catalytic cracking catalyst in a FCC reactor under catalytic cracking conditions to form a cracked product;

5 (b) separating at least a naphtha fraction and a cycle oil fraction from said cracked product, said cycle oil containing aromatic species;

(c) hydroprocessing at least a portion of said cycle oil fraction to convert a substantial portion of said aromatic species in said cycle oil fraction, thereby forming a
10 hydroprocessed cycle oil; and,

(d) introducing said naphtha fraction and said hydroprocessed cycle oil into said FCC reactor at a point upstream from a point at which said hydrocarbonaceous feed is contacted with said catalytic cracking catalyst.

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10. The process according to claim 9 further comprising the step of contacting said naphtha fraction and said hydroprocessed cycle oil with said catalytic cracking catalyst.

11. The process according to claim 10 wherein said naphtha fraction and said
20 hydroprocessed cycle oil are introduced at a rate sufficient to keep the weight ratio of the naphtha fraction and hydroprocessed cycle oil to catalyst between about 1 and 100.

12. The process according to claim 11 wherein the weight ratio of said naphtha fraction to hydroprocessed cycle oil is between about 1 and 10.

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13. The process according to claim 12 wherein the weight of said aromatic species in said hydroprocessed cycle oil is less than or equal to about 1 wt.% of the total weight of the hydroprocessed cycle oil introduced into said FCC reactor upstream from said point at which said hydrocarbonaceous feed is contacted with said catalytic cracking
30 catalyst.

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14. The process according to claim 13 further comprising the step of separating said cracked product from said catalyst.

15. The process according to claim 14 further comprising the step of stripping said catalyst.

16. The process according to claim 15 further comprising the step of regenerating said catalyst.

17. The process according to claim 16 further comprising the step of introducing a regenerated catalyst into said FCC reactor.

18. The process according to claim 1 wherein said naphtha fraction and said hydroprocessed cycle oil are injected into said second reaction zone at a rate sufficient to keep the weight ratio of the total naphtha fraction and hydroprocessed cycle oil to said catalyst between about 1 and 5.

19. The process according to claim 13 wherein said naphtha fraction and said hydroprocessed cycle oil are injected into said second reaction zone at a rate sufficient to keep the weight ratio of the total naphtha fraction and hydroprocessed cycle oil to said catalyst between about 1 and 5.

20. The process according to claim 1 wherein the weight ratio of said naphtha fraction to hydroprocessed cycle oil is between about 3 and 4.

21. The process according to claim 12 wherein the weight ratio of said naphtha fraction to hydroprocessed cycle oil is between about 3 and 4.

22. The process according to claim 1 wherein the weight of said aromatic species in said hydroprocessed cycle oil is less than or equal to about 0.1 wt.% of the total weight of the hydroprocessed cycle oil introduced into said second reaction zone.

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22. The process according to claim 1 wherein the weight of said aromatic species in said hydroprocessed cycle oil is less than or equal to about 0.01 wt.% of the total weight of the hydroprocessed cycle oil introduced into said second reaction zone.

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23. The process according to claim 13 wherein the weight of said aromatic species in said hydroprocessed cycle oil is less than or equal to about 0.1 wt.% of the total weight of the hydroprocessed cycle oil introduced into said FCC reactor upstream from said point at which said hydrocarbonaceous feed is contacted with said catalytic

10 cracking catalyst.

24. The process according to claim 13 wherein the weight of said aromatic species in said hydroprocessed cycle oil is less than or equal to about 0.01 wt.% of the total weight of the hydroprocessed cycle oil introduced into said FCC reactor upstream from said point at which said hydrocarbonaceous feed is contacted with said catalytic

15 cracking catalyst.