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(71) **Applicant** *(for all designated States except US)*: **EXXONMOBIL CHEMICAL PATENTS INC.** [US/US]; 5200 Bayway Drive, Baytown, TX 77520-2101 (US).

(72) **Inventors; and**
(75) **Inventors/Applicants** *(for US only)*: **KEUSENKOTHEN, Paul, F.** [US/US]; 408 Hawthorne Street, Houston, TX 77006 (US). **IACCINO, Larry, L.** [US/US]; 2409 Menard Street, Seabrook, TX 77586 (US). **SEARLE, Ronald, G.** [AU/QA]; 14 Waterfalls Avenue, Doha (QA). **DAVIS, Mark, S.** [US/US]; 8102 Clearwater Crossing, Humble, TX 77396 (US).

(74) **Agents**: **HUGHES, Gerard J.** et al.; Exxonmobil Chemical Company, Law Technology, P.O. Box 2149, Baytown, TX 77522-2149 (US).

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(54) **Title**: COKE GASIFICATION ON CATALYTICALLY ACTIVE SURFACES

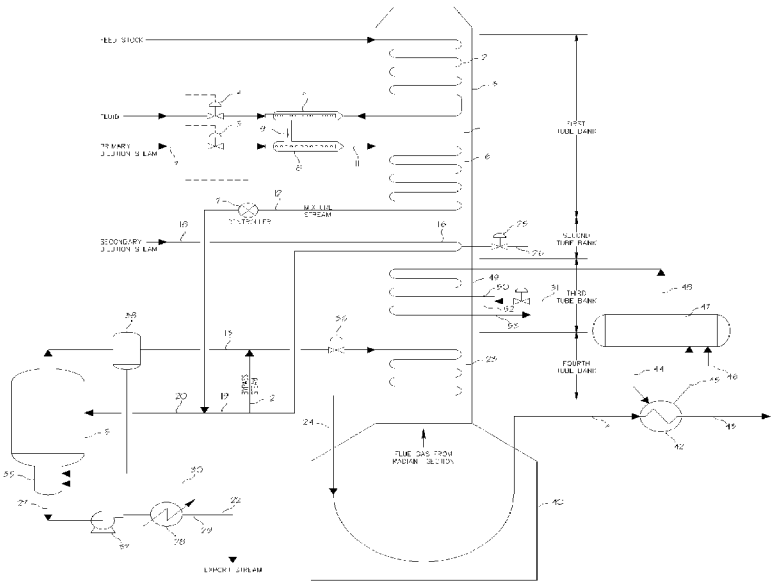


Figure 2

(57) **Abstract**: A method and system for converting hydrocarbons into C_{2+} unsaturates is described. The method includes providing a structural member upstream of a reaction zone having a surface of a catalytic material, wherein the catalytic material is rendered catalytically active to promote the reaction of coke and/or coke precursors with hydrogen (H_2) and/or an oxidant. Then, the method involves exposing a hydrocarbon stream to the catalytic material, wherein the hydrocarbon stream comprising coke and/or coke precursors react in the presence of the catalytic material to convert at least a portion of the coke and/or coke precursors to vapor products. Finally, the hydrocarbons in the hydrocarbon stream containing vapor products and hydrocarbons are converted in the reaction zone to produce a reactor product having C_{2+} unsaturates.

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COKE GASIFICATION ON CATALYTICALLY ACTIVE SURFACES

PRIORITY CLAIM

[0001] This application claims priority to and the benefit of USSN 61/488,462, filed May 20, 2011 and European Application No. 11177020.2, filed on August 9, 2011.

FIELD

[0002] This invention relates to processes and apparatuses for inhibiting coke deposition within hydrocarbon processing system which is subject to fouling.

BACKGROUND

[0003] Many apparatus used in the processing of petroleum have a tendency to become fouled by deposits of coke necessitating occasional removal from service for cleaning. Coke includes carbonaceous material with low hydrogen content present as a solid, semi-solid and/or viscous liquid. Different mechanisms may lead to coking in the vapor phase and/or in the liquid phase. For the vapor phase, coking may form from deposits of low volatility materials and/or from chemical reactions, which may be on a surface of equipment exposed to the hydrocarbon streams and may include Diels-Alder and free radical condensation/oligomerization reactions. For the liquid phase, coking may occur from chemical reactions and from the deposition of insoluble materials.

[0004] As an example, deposition of low volatility materials may occur at locations where a hydrocarbon stream is being heated and the majority of the stream vaporizes (e.g., the "dry point"), may occur when high molecular weight species form in the vapor phase, and/or may occur when the stream is being cooled and some molecules begin to condense (e.g., the "dew point"). If this deposition occurs on the internal surface of equipment, such as a heat exchanger or reactor components, the walls of the equipment are coated with deposits that result in operational difficulties. These difficulties include: (i) diminished heat transfer rate between the wall and the material in the tube; (ii) deterioration of temperature regulation, (iii) development of flow restrictions that may cause increased pressure drop and/or maldistribution; (iv) increase in shut-downs and cleaning cycles, which may be challenging for long or complex components (e.g., the more expensive and difficult is the cleaning job); and/or (v) damage to the equipment result. As such, coking for hydrocarbon processing facilities results in reduced operation inefficiencies, such as downtime for cleaning, reduced throughput, and increased energy inefficiencies, along with the expense of decoking operations.

[0005] The periodic cleaning involves interrupting normal operations (e.g., hydrocarbon processing operations), taking the equipment out of service for decoking operations, and restarting the normal operations once the cleaning is complete. The decoking or cleaning operation includes various chemical or mechanical methods, which are typically labor intensive, add significantly to the maintenance cost of the equipment and often requires replacement of the major components. The most common means of cleaning coked equipment is to combust the coke with air that may be diluted with steam, nitrogen, or other material to reduce the oxygen content thereby lowering and/or controlling the temperature of decoking operations.

[0006] To minimize the difficulties with coking, certain references describe using certain materials for the components in the reaction zone to make surfaces more chemically inert, reduce adhesion in the reaction zone or downstream of the reaction zone, and/or provide additives to the hydrocarbon stream to mitigate coking. For example, using stainless steel in the radiant section of a reactor has been described to have a lower tendency to form coke during use. Specifically, U.S. Patent Nos. 5,630,887 and 6,436,202 describe the use of stainless steel for furnace tubes.

[0007] Similar to the use of stainless steel for furnace tubes, other references describe the use of various surface coatings in the reaction zone, such as U.S. Patent Nos. 6,824,883; 7,056,399 and 7,488,392 and U.S. Published Patent Application Nos. 2007/0105060; 2008/0073063 and 2009/0011925. As a specific example, one such coating involves forming a protective surface film by depositing a layer of silica resulting from oxidative decomposition of an alkoxy silane in the vapor phase on the metal surface. U.S. Patent No. 6,899,966 describes a composite surface having a thickness from 10 to 5,000 microns comprising a spinel of the formula $Mn_xCr_{3-x}O_4$ wherein x is from 0.5 to 2 and oxides of Mn, Si selected from the group consisting of MnO, $MnSiO_3$, Mn_2SiO_4 and mixtures thereof which are not prone to coking and are suitable for hydrocarbyl reactions, such as furnace tubes for cracking. Another coating involves a layer that is from several microns to several millimeters thick of a ceramic material deposited by thermal decomposition of a silicon containing precursor in the vapor phase. This coating is used to passivate a reactor surface subject to coking. Further, surface coatings of alumina have also been explored to reduce coking by making the surface less catalytically active. The alumina surface coating may be formed by deposition and/or aluminum incorporation into the metallurgy so that aluminum can migrate to the surface and oxidize to form an alumina layer. These approaches result in a surface

oxide, which is less likely to catalyze the production of some coke, but the surfaces have relatively high surface energy that attracts unwanted deposits (already present and/or formed in the vapor phase) to the surface. Other coatings may be based on polymeric materials, such as polyethylene and polyvinylfluoride, with low surface energy, such as the coatings used to perform at lower temperatures. However, these polymeric coatings generally can not withstand higher temperatures typically involved with hydrocarbon processing and are not effective to reduce coking.

[0008] These surface coating approaches, such as silica and alumina oxide, generally involve forming a layer on the surface of conduits in the micron to millimeter range in thickness. This is usually to ensure good surface coverage as well as provide a protective layer of sufficient thickness to be robust during operating conditions. Coatings of such thickness may, however, limit heat transfer. Treatments with silicate sols, or paints rich in silicon or aluminum typically produce relatively thick surfaces (micron to millimeter) that can provide a physical boundary that protects the underlying metal from corrosion. However, such treatments do not have low surface energies if the surface terminates in an oxide/hydroxide surface layer. The use of silanes for chemical vapor deposition is also known, but with the intent to diffuse Si, C, H and other elements into the metal surface using high temperatures (e.g. 600°C); the result is that the surface, though non-metallic, can still have a high surface energy and does not reject coke. Thus, conventional treatments tend to be inadequate either because they are too thick for good heat transfer or, alternatively, do not adequately resist coke.

[0009] With regard to the additives in the hydrocarbon stream, various on-stream additives have also been explored to reduce coke production. For example, sulfur (typically added as H_2S) is described as reducing coking in steam cracking and aromatics reforming. Phosphorous has been also utilized to reduce coking. While only partially effective, these additives require ongoing addition and may result in product clean-up requirements. Accordingly, other approaches may be preferred to the additive operations.

[0010] There is a need to reduce and/or eliminate fouling in petroleum refining apparatuses, which is presently not adequately addressed by the prior art.

SUMMARY

[0011] In one embodiment of the present techniques, a method of converting hydrocarbons into C_{2+} unsaturates is described. The method of converting hydrocarbons into C_{2+} unsaturates comprising: providing at least one structural member upstream of a reaction

zone at least a portion of the inner surface of such member comprising a catalytic material that promotes the reaction of coke and/or coke precursors with hydrogen (H_2) and/or an oxidant to form vapor products; exposing a hydrocarbon stream that contains coke and/or coke precursors to the catalytic material in the presence of hydrogen and/or an oxidant and reacting at least a portion of the coke and/or coke precursors to form vapor products; and converting at least a portion of the hydrocarbon stream containing the hydrocarbons and the vapor products in the reaction zone to produce a reactor product having C_{2+} unsaturates.

[0012] In another embodiment, a pyrolysis system is described. The pyrolysis system comprising a pyrolysis unit having a reaction zone, wherein the pyrolysis unit is configured to convert hydrocarbons into C_{2+} unsaturates; and at least a portion of a surface of at least one structural member upstream of the reaction zone having a catalytic material thereon that promotes the reaction of coke and/or coke precursors with hydrogen (H_2) and/or an oxidant. The pyrolysis (e.g., thermal cracking) may comprise exposing the hydrocarbon stream to temperatures in the range of 1200°C to 2200°C, where greater than 75 % of heat for the converting may be provided via indirect heat transfer.

[0013] In yet another embodiment, another method of converting hydrocarbons into C_{2+} unsaturates is described. The method comprising: converting a hydrocarbon stream in a reaction zone of a regenerative reverse flow reactor to produce a reactor product comprising C_{2+} unsaturates and hydrogen (H_2); exposing at least a portion of the reactor product to at least a portion of a surface of at least one structural member having the catalytic material thereon that promotes the reaction of coke and/or coke precursors with hydrogen (H_2) and/or an oxidant at temperatures greater than 150°C; and reacting in the presence of the catalytic material at least a portion of the coke and/or coke precursors with the hydrogen (H_2) and/or oxidant to convert the coke and/or coke precursors to vapor products.

[0014] Further still, in other embodiments, another pyrolysis system is described. The pyrolysis system may include a regenerative reverse flow reactor having a reaction zone, wherein the regenerative reverse flow reactor is configured to convert hydrocarbons into C_{2+} unsaturates; and at least one structural member downstream of the reaction zone having at least one surface of a catalytic material, wherein the catalytic material promotes the reaction of coke and/or coke precursors with hydrogen (H_2) and/or an oxidant to form vapor products.

[0015] In yet another embodiment, a method of converting hydrocarbons into C_{2+} unsaturates is described. The method comprising converting a first hydrocarbon stream into a

reactor product comprising C_{2+} unsaturates and coke in a reaction zone of a regenerative reverse flow reactor having a reactor bed and at least one structural member adjacent to an end of the reactor bed, wherein such structural member comprises one or more of a removal component and a injection component, and wherein at least a portion of the inner surface of such structural member comprises a catalytic material that promotes the reaction of coke with an oxidant; removing a first portion of the reactor product from the reaction zone; exposing a second portion of the of the reactor product to (i) the catalytic material and (ii) an oxidant in a stoichiometric excess amount required to react with the coke; reacting the coke and the oxidant in the presence of the catalytic material to convert at least a portion of the coke to vapor products; exothermically reacting the remaining oxidant with a fuel stream in the reaction zone to produce a combustion product; and removing at least a portion of the combustion product prior to the providing a second hydrocarbon stream to the reaction zone.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Fig. 1 illustrates a diagram of partial O_2 pressure in equilibrium with steam with various amounts of hydrogen (H_2).

[0017] Fig. 2 illustrates a schematic flow diagram of an exemplary embodiment with a steam cracker system in accordance with an embodiment of the present techniques.

[0018] Fig. 3 is a diagrammatic illustration of an exemplary regenerating reverse flow reactor system in accordance with another embodiment of the present techniques.

[0019] Fig. 4 is a diagrammatic illustration of an exemplary pyrolysis reactor system having a pulsed compression reactor in accordance with yet another embodiment of the present techniques.

DETAILED DESCRIPTION

[0020] In the processing of hydrocarbons, the coking mechanisms that are associated with inefficiencies in hydrocarbon processing involve chemical reactions and the deposition of insoluble materials. In these mechanisms, the reduction of the viscous sub-layer (or boundary layer) close to the surface (e.g., inner wall or surface of a piece of equipment) may mitigate the coking rate. The inner surface may be a surface that is within the reactor or exposed to one or more streams in the process. In chemical reactions, certain temperatures at the surface of a heat transfer surface may activate molecules to form precursors for the fouling residue (e.g. coke). If these coke precursors are not swept out of the relatively stagnant surface region, the coke precursors may associate together and deposit on the surface. A reduction of the boundary layer reduces the thickness of the stagnant region and

hence the amount of precursors available to form coke deposits. For the deposition of insoluble materials, a reduction in the boundary layer increases the shear near the surface and hence exerts a greater force on the insoluble particle near the surface to overcome the particle's attractive forces to the surface, which reduces the probability of deposition and incorporation into any residue.

[0021] Coke is a carbonaceous material that may be a tar, semisolid or solid at process conditions (e.g., certain temperatures, pressures and environments), which is typically formed by chemical reactions, such as condensation, oligomerization or polymerization of unsaturated hydrocarbons formed by the process, and/or the deposition of insoluble materials, such as non-volatile (e.g., asphaltenes) or multi-ring aromatic species. In numerous processes, coke formation occurs even though coke is not a thermodynamically stable species at the process conditions. For example, coke includes solid materials that are predominately carbon (C), but may contain some hydrogen (H) and other atomic species (e.g., sulfur (S), nitrogen (N), oxygen (O), halogens, etc). Structurally, the coke may be well ordered graphitic type materials to amorphous materials and also include viscous liquid materials that are precursors to solid coke (coke precursors). Accordingly, various factors contribute to the formation of coke on the surfaces within a system, such as process conditions, process environment, and feed composition, for example.

[0022] Formation of coke is especially troublesome in processes used to produce C_{2+} unsaturates (e.g., ethylene, acetylene, propylene, benzene along with other olefins and aromatics) from hydrocarbons. These processes include various heating and separating units for feed pretreatment, a pyrolysis unit (e.g., reactor or furnace) for converting the hydrocarbons in the feed into C_{2+} unsaturates in a reaction zone and recovery units to process the resulting products. The term "reaction zone" means a location in the pyrolysis system where greater than 50%, greater than 75% and/or greater than 90% of the conversion of hydrocarbons into C_2 unsaturates in the pyrolysis system is performed. That is, while some thermal cracking may occur upstream of reaction zone, the reaction zone is the location where a substantial amount of the smaller molecules are produced from the initial hydrocarbons to the system. For example, the reaction zone for a steam cracking system is in the radiant tubes of the steam cracking furnace. The reaction zone for a regenerative reverse flow reactor is the central location, which may include a portion of the reactor beds near the central location.

[0023] Regardless of the specific process, cracking of hydrocarbons entails heating hydrocarbons in the presence of optional fluids (e.g., steam or other fluids, such as hydrogen) to various temperatures that convert the hydrocarbons in the reactor feed into C_{2+} unsaturates. For certain pyrolysis processes, such as indirect heat transfer, the process involves heating a solid material (e.g., by combustion) and using the heated solid material to crack the hydrocarbons. For indirect heat transfer processes, the combustion products are maintained separate from the hydrocarbon stream. This technique involves various different types of reactors, such as a regenerative reverse flow reactor and/or steam cracking. Typically, steam cracking may heat the hydrocarbons in the reactor feed to process conditions that include a temperature in excess of about 370°C and at pressures greater than 25 psia, as disclosed in U.S. Patent No. 7,138,047. A\ regenerative reverse flow reactor may heat the hydrocarbons in the reactor feed to process conditions that include temperatures in excess of 1200°C, in excess of 1500°C, in excess of 1700°C, and even in excess of 2000°C, and at a variety of pressures, such as at pressures in the range of 3 psig (21 kPa) to 162 psig (1117 kPa) and/or in the range of 15 psig (103 kPa) to 103 psig (710 kPa). At such process conditions, many of the hydrocarbon molecules undergo cracking, that is, the breaking of carbon-carbon bonds and/or releasing hydrogen from saturates to form ethylene, acetylene and propylene, among other olefinic and aromatic products. Through undesirable side reactions, equipment surfaces (e.g., surfaces or walls of furnace tubes, other process tubes and/or components) gradually accumulate carbonaceous deposits (e.g., coke), which eventually may cause an unacceptable increase in pressure drop and loss of heat transfer in the process.

[0024] The process conditions may also include a process environment that may be net-reducing or net-oxidizing, but may also include an environment that both oxidation and reduction reactions are possible. Oxidation-reduction reactions, which may be referred to as redox reactions, describe chemical reactions in which atoms have their oxidation number (oxidation state) changed. That is, redox reactions include oxidation reactions, which is the loss of electrons or an increase in oxidation state by a molecule, atom, or ion; and reduction reactions, which involves the gain of electrons or a decrease in oxidation state by a molecule, atom, or ion. These reactions may be either a simple redox process, such as the oxidation of carbon to yield carbon dioxide (CO_2) or the reduction of carbon by hydrogen to yield methane (CH_4).

[0025] Another factor in the coke formation is the composition of the stream at the respective location along the flow path within the system (e.g., present within the equipment).

As an example, the pyrolysis unit may involve a hydrocarbon feed that includes various hydrocarbons and have a hydrogen content of in the range of 8 wt% to 25 wt% of the hydrocarbons of the hydrocarbon feed, in the range of 12 wt% to 25 wt% of the hydrocarbons of the hydrocarbon feed, in the range of 12 wt% to 20 wt% of the hydrocarbons of the hydrocarbon feed and/or in the range of 20 wt% to 25 wt% of the hydrocarbons of the hydrocarbon feed.

[0026] The present techniques utilize catalytically active surfaces to enable a kinetic pathway at steady state and/or transient reaction conditions so that coke and/or coke precursors can be removed and/or the formation can be prevented. The catalytically active surface may be bulk metallurgy; addition of active species to surface of bulk metallurgy; or coatings added to and/or bonded to the bulk metallurgy. The bulk metallurgy is the process equipment (e.g., tube or vessel). As an example, the catalytic species (for H_2 gasification or oxidation of coke) may be incorporated into a glass-like, catalytically active coating for the interior (e.g., in contact with the process streams) of process equipment to prevent coke fouling of the equipment. For H_2 gasification of the coke and/or coke precursors, this catalytic route approach may be applicable to process equipment and process conditions where H_2 is sufficient at the partial pressure so that the thermodynamically favored route is for H_2 to react with coke or coke precursor to produce methane or other light hydrocarbons and not in a thermodynamic regime so that instead hydrocarbon decomposition to coke and H_2 occurs. The process conditions may be adjusted (e.g., amount of H_2 added to the stream, total pressure, and/or temperature) to be in the proper regime. Choice of catalytic material and process conditions may also be such that an extensive amount of hydrogenation of desired feeds and products does not occur. Some of the potential applications for this aspect are steam cracking radiant section tubes; heat exchangers (e.g., transfer line exchangers (TLE's)); cokers; hydrotreater preheat furnaces; separators or other equipment, as discussed further below.

[0027] To reduce the potential for coking at various locations, coke deposition may be inhibited by depositing a catalytically active species onto the internal surfaces of hydrocarbon processing equipment to provide kinetic pathways for the reactions involving coke and/or coke precursors based on the process environment (e.g., oxidizing environment or reducing environment) and other process conditions. The catalytic material may be an active material or capable of becoming active at process conditions. Various different pyrolysis systems (e.g., steam cracking systems or regenerative reverse flow reactors) may benefit from having

surfaces of structural members or components coated with the catalytic material. These pyrolysis systems may include pyrolysis units (e.g., thermal reactors, such as a steam cracking reactor and a regenerative reverse flow reactor, and/or other reactors) to perform the conversion in a reaction zone. Further, associated equipment may also benefit from having various surfaces of structural members coated with the catalytic material (e.g., a catalytically active species). The associated equipment may include heat exchangers, separators, and different tubes (e.g., piping or conduits) connecting the equipment or other suitable equipment that may be subject to coking. The catalytic material may provide a surface net coke deposition rate is less than 1.0 $g/m^2/hr$, less than 0.1 $g/m^2/hr$, less than 0.01 $g/m^2/hr$ or less than 0.001 $g/m^2/hr$.

[0028] Internal surfaces of process equipment (e.g., surfaces of reactor components or other structural members) subject to coking may have a catalytic material containing or consisting of an oxidation catalyst and/or hydrogenation catalyst. As an example, the catalyst may include Group IB, IIB, IIIA, IVA, IVB, VB, VIB, VIIB and/or VIIIB metal oxides or sulfides of The Periodic Table of Elements. The "Periodic Table of the Elements" means the Periodic Chart of the Elements as tabulated on the inside cover of The Merck Index, 10th Edition, Merck & Co., Inc., 1983. The catalyst may preferably be selected from the group consisting of Al, Ag, Au, Co, Cr, Cu, Fe, Ir, Mo, Mn, Nb, Ni, Pd, Pt, Re, Ru, Rh, Sn, W, Zn, and alloys and mixtures thereof. Specifically, the catalyst may include sulfides and oxides from Group VIIIB, such as Co, Ni, Pt and Pd.

[0029] As another example, the catalyst may include MAX phase catalytic materials, which are ternary carbides and nitrides with the general formula $M_{n+1}AX_n$, where n = 1 to 3, M is an early transition metal (e.g., Group IIIB-VIB), A is an A-group element (e.g., Group IIIA-VIA), and X is carbon (C) and/or nitrogen (N). The catalyst may preferably be selected from the Group consisting of Sc, Ti, V, Cr, Zr, Nb, Mo, Hf, Ta and mixtures thereof. Specifically, the catalyst may include Ti_2AlC, Ti_2AlN, Hf_2PbC, Cr_2GaC, V_2AsC, Ti_2InN, Nb_2AlC, $(Nb,Ti)_2AlC$, $Ti_2AlN_{0.5}C_{0.5}$, Nb_2GaC, Nb_2AsC, Zr_2InN, Ti_2GeC, Cr_2AlC,Ta_2AlC, V_2AlC, V_2PC, Nb_2PC, Ti_2PbC, Zr_2SnC, Hf_2SnC, Ti_2SnC, Nb_2SnC, Zr_2PbC, Zr_2SC, Ti_2SC, Nb_2SC, Hf_2SC, Ti_2GaC, V_2GaC, Mo_2GaC, Ta_2GaC, Ti_2GaN, Cr_2GaN, V_2GaN, V_2GeC, Sc_2InC, Ti_2InC, Zr_2InC, Nb_2InC, Hf_2InC, Hf_2InN and/or Hf_2SnN.

[0030] As yet another example, the catalyst may include a catalytically active multi-phase glass-ceramic precursor, which when melted and devitrified forms a catalytically active polycrystalline ceramic; or the catalytic material may be created by bulk metallurgy, such as

by the addition of catalytically active species to surface of bulk metallurgy; or coatings added to and/or bonded to the bulk metallurgy. The term "primary crystalline phase" refers to that portion of a catalytically active glass-ceramic comprising greater than 50% by volume of the glass-ceramic. As used herein, the term "secondary crystalline phase" refers to a crystalline portion of a catalytically active glass-ceramic comprising less than 50% by volume of the glass-ceramic. The term "secondary noncrystalline phase" refers to a noncrystalline portion of a catalytically active glass-ceramic comprising less than 50% by volume of the glass-ceramic, and the term "catalyst precursor" refers to a material which is converted into a catalyst material after processing. For example, metal oxides are catalyst precursors which are converted into catalysts upon exposure to a reducing atmosphere, or the catalyst precursors may be metal silicates. As used herein, the term "glass-ceramic precursor formulation" refers to a combination of materials (raw glass batch) suitable for melting to form amorphous glass, and the term "glass-ceramic precursor material" refers to the amorphous glass produced by melting the raw glass batch. The glass-ceramic precursor material can comprise silicates (e.g., lithium silicate and aluminosilicates, such as lithium aluminosilicate).

[0031] Coke deposition may be inhibited by a reduction of the hydrocarbon coke in the presence of hydrogen and these catalytically active surfaces. The catalyst materials may be incorporated into polycrystalline ceramic materials. For example, U.S. Published Patent Application No. 2009/0011925 describes materials that are catalytically active glass-ceramic materials. These materials comprise a primary crystalline matrix which may contain a relatively small amount of catalytically active metal, at a secondary crystalline phase and a secondary noncrystalline phase located at a boundary of the primary crystalline phase, and at least one catalytically active metal disposed in at least one of the secondary crystalline phase and the secondary noncrystalline phase.

[0032] The catalytic material may be a layer formed in a structural member or applied to the structural member. That is, the catalyst material may be formed into the bulk metallurgy of the structural member, such as on the interior of tubes (e.g., piping or conduits) for use in the various hydrocarbon processing systems which are subject to coking. The catalytic material may be formed via absorption, implantation, chemical deposition and/or other processes. As another approach, the catalytic material may be a coating of catalytic material along with other materials, such as binding materials, which are disposed on a portion of the equipment that provides physical form or shape for the surface. The structural member may be at least a portion of a tube, at least a portion of equipment (e.g., reactor housing, manifold,

reactor tiles, heat exchanger and/or separator) and/or at least a portion of a component (e.g., honeycomb monolith, mixer, valve and piston). The catalytic material may be applied to the structural member through any known technique, such as sponging, painting, deposition and/or spraying, for example. The thickness of the catalytic material may be in the range of 5 microns to 1500 microns, 20 microns to 1200 microns, 30 microns to 1100 microns.

[0033] The composition of the catalytic material may include an active catalytic component concentration ranging between 100 ppm to 10 wt%. Glass-ceramic has a crystal content of at least about 10% by volume and the majority of the crystals forming the glass-ceramic preferably have a crystal size less than about 10 microns. In one preferred embodiment, the glass-ceramic is an aluminosilicate having a composition comprising a range of about 35 wt% to 75 wt% SiO_2, 12 wt% to 25 wt% Al_2O_3, 5 wt% to 30 wt% of at least one of NiO, CoO, and FeO, 0 wt% to 10 wt% Li_2O, 0 wt% to 10 wt% MgO, 0 wt% to 5 wt% CaO, 0 wt% to 3 wt% B_2O_3, 0 wt% to 3 wt% ZnO, 0 wt% to 15 wt% CeO_2, and 0 wt% to 5 wt% of at least one of TiO_2 and ZrO_2.

[0034] Catalytic surface activity should be such that at the process conditions (e.g., temperature and O_2 or H_2 partial pressure present at the surface), reaction of coke and or coke precursors occurs, but minimal amount of valuable feed or product hydrocarbons are converted by the active catalytic decoking material. That is, the catalytic material may preferably be a weakly active material.

[0035] Accordingly, the process environment may be a reducing environment (e.g., net-reducing) or an oxidation environment (e.g., net-oxidizing). As noted above, process environments with an excess of hydrogen (H_2) are reducing environments. While coke may still form as a kinetic product even when it is not thermodynamically stable, the addition of a suitable catalyst may enable the increase in the kinetic rate for coke reduction to methane. Similarly, process environments with an excess of oxygen (O_2) relative to hydrogen H_2 are oxidizing environments. As with reducing environments, coke may be present as a kinetic product even when it is not thermodynamically stable. The addition of a suitable catalyst may increase the kinetic rate for coke oxidation to carbon monoxide (CO) and/or carbon dioxide (CO_2) in the oxidizing environment. Oxygen (O_2) may be supplied to the process as molecular O_2 or may be supplied as an oxidized species, such as H_2O or CO_2, which may act as sources of oxidant (e.g., $H_2O = H_2 + ½\ O_2$ and $CO_2 = CO + ½\ O_2$). Regardless, it may be referred to as an oxidant.

[0036] In addition, a hydrogen (H_2) containing stream may be combined with the hydrocarbon stream (e.g., hydrocarbon feed) to form a reactor feed. The hydrogen (H_2) containing stream may include hydrogen gas (H_2) in an amount that provides a preferred ratio of hydrogen gas (H_2) moles to the total moles of carbon (C) in the hydrocarbon components of the reactor feed. Hydrogen gas can be added in pure form, or in the form of gas mixtures which are produced in various refinery processes. The ratio of hydrogen to carbon (H_2/C) may be from 0.0 or 0.1 to 5.0, such as 0.0, 0.1, 1.0, 2.0, 3.0, 4.0, 5.0, or values in between for the reactor feed. Combining the hydrogen content of the hydrogen gas to the hydrogen and carbon contents of the hydrocarbon components of the hydrocarbon feed may result in a total atomic ratio of hydrogen (H) to carbon (C) in the reactor feed that is from 3 to 15. The weight percent of total hydrogen in the reactor feed may be greater than that in the hydrocarbon feed. For example, the weight percent of total hydrogen in the reactor feed may be between 8 wt% and 54 wt%. In certain embodiments of the process, H_2 should be added or maintained at levels of greater than about 0.1 mole%, greater than 1.0 mole%, or even greater than 2.0 mole%, but less than 5.0 mole%, 4.0 mole%, or even less than 3.0 mole%.

[0037] As an example, Fig. 1 illustrates a diagram of partial O_2 pressure in equilibrium with steam with various amounts of H_2. In diagram 100, various response curves 108-114 of partial O_2 pressure for a given temperature are shown based on the values for O_2 partial pressure (in psia) along the Y1-axis 104, different temperatures (in °C) along the x-axis 102, and different H_2 pressures (in psia) along the Y2-axis 106. The response curve 108 is associated with 0 psia of H_2 being added to 40 psia of steam, the response curve 110 is associated with 0.1 psia of H_2 being added to 39.9 psia of steam, the response curve 112 is associated with 1 psia of H_2 being added to 39 psia of steam, and the response curve 114 is associated with 10 psia of H_2 being added to 30 psia of steam. The addition of hydrogen (H_2) in these response curves 110-114 indicates that partial O_2 pressure may be dramatically reduced for lower temperatures. This effect is specifically present at temperatures below 850°C, even more at temperatures below 550°C. In addition, the response curves 110-114 indicate that a reducing environment may be provided with between 0 psia and 0.1 psia of hydrogen (H_2) being added to the steam. As such, the process environment may be adjusted by the addition of H_2 to further inhibit coking on surfaces at certain locations.

[0038] Further, in certain embodiments of the present techniques, it is possible that the hydrogen (H_2) containing stream is from a relatively low purity hydrogen sources, such as synthesis gas and/or refinery fuel gas. The synthesis gas (i.e. syngas) includes H_2 and carbon

monoxide (CO) and may also include various levels of carbon dioxide (CO_2), nitrogen (N_2), water (H_2O), light hydrocarbons, and/or hydrogen sulfide (H_2S) as well as other contaminants. The refinery fuel gas may include H_2 and methane (CH_4) and may also include various levels of CO, CO_2, N_2, H_2O, light hydrocarbon, and/or H_2S as well as other contaminants. The hydrogen (H_2) containing stream may be added to the hydrocarbon stream at any suitable point in the systems upstream of or into locations where coking may occur.

[0039] Another addition to the hydrocarbon stream may include an oxidant stream. As noted above, the oxidant stream may include oxygen gas in pure form, or more preferably in the form oxidants, such as H_2O and/or CO_2. The oxidant may be provided in an amount that provides a preferred ratio of oxygen (O) moles to the total moles of carbon (C) in the hydrocarbon components of the reactor feed. The ratio of oxygen to carbon (O/C) may be from 0.0 or 0.01 to 0.6, such as 0.0, 0.01, 0.1, 0.15, 0.2, 0.4, 0.6, or values in between.

[0040] According to certain embodiments of the present techniques, the catalyst (e.g., hydrogenation catalyst and/or oxidation catalyst) may be utilized in a process environment (e.g., reducing environment or oxidizing environment) upstream of the reaction zone for a reactor system. That is, the catalyst may be applied at locations upstream of the reaction zone (e.g., radiant tubes for a steam cracker or central location within a regenerative reverse flow reactor) to enhance the process under certain process conditions and process environments. In particular, the catalyst may form a layer on the surface of at least a portion of a tube or equipment upstream of the reaction zone to reduce coking in these regions.

[0041] By providing a catalytically active material upstream of the reaction zone, the hydrocarbon stream being provided to the reaction zone may be subjected to partial cracking conditions (e.g., higher temperatures and/or pressures, which may include visbreaking conditions) upstream of the reaction zone. This may enhance the process by maximizing the amount of hydrocarbons being separated from an initial feed prior to the reaction zone, while minimizing the coking problems at the upstream locations.

[0042] The term "visbreaking" as used herein is a well-known, non-catalytic, mild thermal cracking process that uses heat to convert or crack heavy hydrocarbonaceous oils and resids into lighter, sometimes more valuable products, such a naphtha, distillates, and tar, but not so much heat as to cause carbonization. The hydrocarbon stream may be heated, such as in a furnace or soaker vessel to a desired temperature, as a desired pressure. The process used may be, for example, the coil type, which provide for high temperature-short residence time, or the soaker process, which provides for lower temperature - longer residence time

processing, as appropriate to obtain the desired broken product mix. The hydrocarbon feed stream may be heat soaked to reduce the viscosity and chain length of the hydrocarbon molecules, by cracking the molecules in the liquid phase. *See*, for example, Hydrocarbon Processing, September 1978, page 106. Visbreaking occurs when a heavy hydrocarbon, or resid, is heat soaked at high temperature, generally from about 700°F (371°C) to about 900°F (371°C to about 482°C) for several minutes before being quenched to stop the reaction. Some of the resid molecules crack or break producing components that can be removed by standard atmospheric and vacuum distillation. Resid conversion in a visbreaker increases with increasing temperature and increasing residence time. High severity visbreaking maximizes conversion of 1050°F+ resid and is accomplished by soaking the visbreaker feedstock at greater than about 840°F (450°C) for the longest time reasonably possible, without forming substantial coke or carbonization.

[0043] As an example, at least a portion of the hydrocarbon feed containing non-volatile components (e.g., resid) is vaporized, such as during (i) hydroprocessing, (ii) when combined with steam, and/or (iii) when the pressure is reduced or flashed between a hydroprocessing unit and a pyrolysis unit (e.g., a steam cracking furnace). The term "hydroprocessing" as used herein is defined to include those processes comprising processing a hydrocarbon feed in the presence of hydrogen and a catalyst to hydrogenate or otherwise cause hydrogen to react with at least a portion of the feed. This includes, but is not limited to, a process comprising the step of heating a resid-containing hydrocarbon feed stream in a hydroprocessing step in the presence of hydrogen, preferably also under pressure. The catalytically active material may be applied to surfaces within the equipment and tubes upstream of the reaction zone, within the reaction zone and/or within the equipment and tubes downstream of the reaction zone.

[0044] As one embodiment, the present techniques may involve a process environment that is a reducing environment. That is, the hydrocarbon processing system is operated in the presence of H_2, which is either added or formed *in situ*, such as by a hydrotreater preheat furnace or other unit, for example. Other hydrocarbon processing systems are conventionally operated in the absence of H_2, such as steam cracking furnaces, cokers and their associated tubes and subsystems. By adding H_2 to the process streams in these systems and/or subsystems, coking can be inhibited through catalytic hydrogenation of coke in the presence of various well-known hydrogenation catalyst materials. The hydrogen (H_2) containing stream may include the compositions noted above.

[0045] For catalytic reaction that involves hydrogen (H_2) gasification of coke, the process conditions, such as the environment, should include H_2 containing stream that is present at sufficient partial pressure so that it is the thermodynamically favored route for H_2 to react with the coke to produce methane or other light hydrocarbons rather than in a thermodynamic regime which favors hydrocarbon decomposition to coke and H_2. That is, the present techniques should optimize the amount of excess hydrogen to provide a reducing environment to react with coke and does not involve the addition of excessive hydrogen. Process environment may be adjusted (e.g., the concentration of H_2) along with the other process conditions (e.g., total pressure and/or temperature) to be in the proper regime. The catalytic material and process conditions should also be such that an extensive amount of hydrogenation of the desired feeds and products does not occur.

[0046] Similar to the discussion of hydrocarbon processing apparatuses and systems that are conventionally operated in the presence of H_2, the process environment may include an oxidizing environment. In these embodiments, an oxidant stream may be added to the hydrocarbon streams in these apparatuses, systems and/or subsystems to inhibit coking through catalytic oxidation of coke in the presence of various well-known oxidation catalyst materials. The oxidant stream may include the compositions noted above.

[0047] For catalytic reaction that involves oxidation of coke, the process conditions should include an oxidant stream that is present at sufficient partial pressure so that it is the thermodynamically favored route for the oxidant to react with the coke to produce carbon monoxide (CO) or carbon dioxide (CO_2) rather than in a thermodynamic regime which favors CO and CO_2 decomposition to coke and CO_2 and/or H_2O. Process environment may be adjusted (e.g., the concentration of oxidant) along with the other process conditions (e.g., total pressure and/or temperature) to be in the proper regime. The catalytic material and process conditions should be maintained so that sufficient oxidation of the coke occurs, but the amount of oxidation of valuable hydrocarbon feed and/or product hydrocarbon molecules is not significant. Significant oxidation of valuable hydrocarbon feed and/or product hydrocarbon molecules is undesirable both because of loss of valuable molecules but also due to the formation of excessive amounts of carbon oxides which are contaminants in the product. The oxidant stream may be adjusted based on the output of contaminates (e.g., CO and CO_2) being generated for the process. Without this optimization, the recovery equipment has to be sized for increased capacity and contaminates have to be managed through the process, which increases system complexity, costs, and inefficiencies.

[0048] According to certain embodiments of the present techniques, the oxidation catalyst may be utilized in an oxidizing environment upstream of the reaction zone for a pyrolysis system. That is, the oxidation catalyst may be applied on surfaces at locations upstream of the reaction zone (e.g., the radiant tubes for a steam cracker) to enhance the process under certain process conditions and process environments. In particular, the oxidation catalyst may form a layer (e.g., a coating on a structural member or formed on an outer layer of the structural member) on at least a portion of the surfaces within tubes or equipment upstream of the reaction zone, within the reaction zone, and/or downstream of the reaction zone. The oxidation catalyst may be utilized to reduce coking in this region. Further, the stream being provided to the reaction zone may be subjected to partial cracking conditions (e.g., higher temperatures and/or pressures, which may include visbreaking conditions) upstream of the reaction zone. By utilizing the oxidation catalyst, the process conditions may be utilized to maximize the amount of hydrocarbons being subjected to the reaction zone, while minimizing the coking problems in the upstream locations.

[0049] The cracking or conversion of the hydrocarbons typically is performed within a reaction zone of a pyrolysis system. This reaction zone may be the radiant tubes for a steam cracking system and/or a central region within a regenerative reverse flow reactor, which may include a portion of the reactor beds. This reaction zone may be the primary location where heat for the chemical conversion of the hydrocarbons is provided, which may result in the formation of coke. This coking may again be influenced by the feed composition, temperatures, etc. For instance, the higher the final boiling point of the reactor feed, the higher the content of species which increase the rate of coking on the equipment surfaces.

[0050] To further enhance the operation of these different systems, it may be desirable to utilize the catalytic coating to reduce or minimize coking. In pyrolysis systems, one location where the catalytically active species can be deposited is on the inner surface of the process tubes or equipment upstream of the reaction zone. As an example, the catalytic coating may be applied to surfaces in a liquid vapor separation unit integrated with the convection section of a steam cracker furnace, in a pulsed compression reactor upstream of a reaction zone or upstream of regenerative reverse flow reactor, in process tubes in the convection section of the steam cracking furnace, and/or in inlet and/or outlet manifolds, tubes and/or reactor components (e.g., valves, mixers, monoliths, pistons and the like) within a regenerative reverse flow reactor. This catalytic coating may be utilized at locations where the stream is exposed to the dry point (e.g., when a mixture having liquid component and solid component

is heated to form a vapor component and a solid component). Other advantageous locations are the inner surfaces of the process tubes in the reaction zone, such as surfaces in radiant section of the steam cracking furnace, and/or locations downstream of the reaction zone, such as the inner surfaces of the process tubes downstream of radiant section or in transfer line exchangers (TLEs).

[0051] As used herein, the "hydrocarbon stream" may include a hydrocarbon feed provided to a pyrolysis system and as it passes through the pyrolysis system. The hydrocarbon stream may have various fluids added to the stream and/or have certain portions removed from the stream as it passes through the system.

[0052] As used herein, the "hydrocarbon feed" contains hydrocarbons (C bound to H) and may contain (i) minor components of heteroatoms (< 10 wt%) covalently bound to hydrocarbons and (ii) minor components of heteroatoms (< 10 wt%) not bound to hydrocarbons (e.g., H_2O), wherein these weight percents are based on the weight of the hydrocarbon feed. The hydrocarbon feed may include, by way of non-limiting examples, one or more of Fischer-Tropsch gases, methane, methane containing streams such as coal bed methane, biogas, associated gas, natural gas and mixtures or components thereof, steam cracked gas oil and residues, gas oils, heating oil, jet fuel, diesel, kerosene, gasoline, coker naphtha, steam cracked naphtha, catalytically cracked naphtha, hydrocrackate, reformate, raffinate reformate, Fischer-Tropsch liquids, natural gasoline, distillate, virgin naphtha, crude oil, atmospheric pipestill bottoms, vacuum pipestill streams including bottoms, wide boiling range naphtha to gas oil condensates, heavy non-virgin hydrocarbon streams from refineries, vacuum gas oils, heavy gas oil, naphtha contaminated with crude, synthetic crudes, shale oils, coal liquefaction products, coal tars, tars, atmospheric resid, heavy residuum, C4's/residue admixture, naphtha residue admixture, cracked feedstock, coker distillate streams, hydrocarbon streams derived from plant or animal matter, and/or any mixtures thereof. The hydrocarbon feed may also include indigenous molecular species that also include atoms other than carbon and hydrogen, such as sulfur containing species, nitrogen containing species, oxygen containing species, halogen containing species, and metal containing species.

[0053] The term “hydrogen content” means atomic hydrogen bound to carbon and/or heteroatoms covalently bound thereto and which excludes molecular hydrogen (H_2) in the hydrocarbon feed expressed as a weight percent based on the weight of the hydrocarbons in the hydrocarbon feed. Hydrogen content as applied to hydrocarbon feed or reactor feed are expressed as an ASTM weight percent of hydrocarbons in the respective feed. The hydrogen

content of hydrocarbon feeds, reactants and products for present purposes can be measured using any suitable protocol, (e.g., ASTM D4808 - 01(2006) Standard Test Methods for Hydrogen Content of Light Distillates, Middle Distillates, Gas Oils, and Residua by Low-Resolution Nuclear Magnetic Resonance Spectroscopy or ASTM D5291 - 10 Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants).

[0054] The term "reactor feed" means the composition, which may be a mixture, subjected to pyrolysis in the reaction zone. In one embodiment, the reactor feed is derived from a hydrocarbon feed and/or stream (e.g., by separation of a portion from the hydrocarbon feed and optional addition of fluids (e.g., diluents)).

[0055] As used herein, “resid” refers to the complex mixture of heavy petroleum compounds otherwise known in the art as residuum or residual. Atmospheric resid is the bottoms product produced in atmospheric distillation when the endpoint of the heaviest distilled product is nominally 343°C, and is referred to as 343°C+ resid. Vacuum resid is the bottoms product from a column under vacuum when the heaviest distilled product is nominally 566°C, and is referred to as 566°C+ (e.g., temperatures above 566°C) resid. The term "nominally" means here that reasonable experts may disagree on the exact cut point for these terms, but probably by no more than +/- 30°C or at most +/- 75°C. This 566°C+ portion contains asphaltenes, which are problematic to the steam cracker, resulting in coking of the surfaces within the furnace.

[0056] As used herein, the expression “non-volatiles” may be defined broadly herein to mean substantially any metal, mineral, ash, ash-forming, asphaltenic, tar, coke, and/or other component or contaminant within the feedstock that does not vaporize below a selected boiling point or temperature and which, during or after pyrolysis, may leave an undesirable residue or ash within the reactor system, which is difficult to remove. Distillation fractions of a feed can be determined via testing methods American Society of Testing and Materials (ASTM) D2887 or D1160.

[0057] The terms "heavy" and "light" in reference to a hydrocarbon fraction refers to the hydrocarbon’s boiling point, with "heavy" referring to fractions having higher boiling point (e.g., boiling at higher temperature) and "light" referring to fractions having lower boiling point. Boiling points, when used to characterize fractions (e.g., fraction heavier than 565°C) are given at atmospheric pressure, although actual distillation may be carried out at reduced temperature and pressure, as is known in the art.

[0058] Non-combustible non-volatiles may include ash, for example. Methods for determining asphaltenes and/or ash may include ASTM methods, such as methods for asphaltenes may include ASTM D-6560 and D-7061 and methods for ash may include ASTM D-189, D-482, D-524, and D-2415. In the context of a feed, non-volatiles are materials that are not in the gas phase (e.g., are components that are in the liquid or solid phase) at the temperature, pressure and composition conditions of the inlet to the pyrolysis unit. For certain pyrolysis units, such as a regenerative reverse flow reactor or other thermal pyrolysis units, non-combustible non-volatiles (e.g., ash; ASTM D-189) in the reactor feed may be preferably limited to $\leq$ 2 parts per million weight (ppmw) on reactor feed, more preferably $\leq$ 1 ppmw. Combustible non-volatiles (e.g., tar, asphaltenes, ASTM D-6560) may be present in the reactor feed for these regenerative reverse flow reactors at concentrations below 10 wt% of the hydrocarbons in the reactor feed, preferably at concentrations below 1 wt%, most preferably at concentrations below 100 ppmw of the total hydrocarbons of the reactor feed to the pyrolysis unit (or ranges in between), as long as the presence of the combustible non-volatiles do not result in excessive (e.g., $\geq$ 2 or $\geq$ 1 ppmw) concentrations of non-combustible non-volatiles. Exemplary embodiments are described further below in Figs. 2-4.

[0059] Fig. 2 is an exemplary embodiment of a steam cracker system that may be utilized in accordance with the present techniques. In this configuration, a furnace 1, which may be any of a variety of furnaces, includes a convection section 3 and a radiant section 40. The convection section 3 includes various convection section tube banks (e.g., first tube bank 2, second tube bank 6, third tube bank 49 and fourth tube bank 23), which may use hot flue gases from the radiant section of the furnace to heat fluids within the respective tube banks.

[0060] Along the flow path through the furnace 1, a hydrocarbon feed may have other fluids added, such as steam and/or other hydrocarbons, to the hydrocarbon stream. For instance, the mixing can be accomplished using any mixing device known within the art, such as a first sparger 4 or second sparger 8 of a double sparger assembly 9. In particular, a fluid may pass through a fluid valve 14 and a primary dilution steam may be passed via primary dilution line 17 through a primary dilution steam valve 15 to be mixed with the heated hydrocarbon feed in the respective spargers 4 or 8 to form a mixture stream in lines 11 and 12, which pass through controller 7. Also, a secondary dilution steam stream 18 can be heated in the superheater section 16 of the convection section, may be combined with water via water line 26 through an intermediate desuperheater 25 (e.g., control valve and water

atomizer nozzle), and mixed with the heated mixture stream. Optionally, the secondary dilution steam stream 18 may be further split into a flash steam stream in flash steam line 19, which is mixed with the heavy hydrocarbon mixture, and a bypass steam stream in bypass line 21, which is mixed with the vapor phase from the flash before the vapor phase is cracked in the radiant section 40. The flash steam stream may be combined with the mixture stream to form a flash stream in flash line 20.

[0061] Along with the addition of certain fluids, certain portions of the hydrocarbon steam may be removed from the process as well. For example, a separator vessel 5 (e.g., flash separator vessel, as exemplified in U.S. Patent No. 7,578,929; 7,488,459; 7,247,765; 7,193,123 and 7,312,371, which are each incorporated herein) may be utilized to separate the flash stream 20 into two phases: a vapor phase comprising predominantly volatile hydrocarbons and steam and a liquid phase comprising predominantly non-volatile hydrocarbons. The vapor phase is preferably removed from the separator vessel 5 as an overhead vapor stream is further processed in a centrifugal separator 38, which removes trace amounts of entrained and/or condensed liquid, before being passed via overhead line 13, vapor phase control valve 36, and crossover line 24 to the radiant section 40 for cracking (e.g., reactor feed). The liquid phase of the flashed mixture stream is removed from a boot or cylinder 35 on the bottom of the separator vessel 5 as a bottoms stream 27. This stream 27 may be further processed in a pump 37 and cooler 28 with the cooled stream 29 being split into a recycle stream 30 and export stream 22.

[0062] Once the stream is exposed to heat in the radiant section 40, the reactor product or effluent may be further processed. For instance, the process may include optional cooling of the effluent from the radiant section 40 in one or more transfer line heat exchangers, a primary fractionator, and a water quench tower or indirect condenser. In this configuration, the effluent may pass via line 41 to a transfer-line exchanger 42 to provide a cooled effluent via quench line 43 for further processing. A utility fluid, such as boiler feed water, may also pass through the transfer-line exchanger 42 to steam drum 47 via lines 44 and 45. The steam drum 47 may be coupled to the third tube bank 49 to generating high pressure steam via lines 48, 50, 52 and 53 and a utility supply line 46. A steam control valve may be coupled between lines 50, 51 and 52 to provide a water source that controls the temperature of the steam.

[0063] To operate, various stages may heat the hydrocarbon stream to different temperatures. For instance, the hydrocarbon stream may be heated to temperatures between about 150°C and 260°C in the first tube bank 2, while the stream may be heated in the second

tube bank to temperatures between 315°C and 540°C, which is also the temperature utilized in the separator vessel 5. The vapor phase from the separator vessel 5 is further heated in fourth or lower convection section tube bank 23 to temperatures between 425°C to 705°C, while the tubes of the radiant section 40 may further expose the vapor phase to temperatures between 600°C and 1000°C. Further, the temperature of the recycled stream via line 30 may be at temperatures between 260°C to 315°C.

[0064] The formation of coke and/or coke precursors may be a problem for certain within this system. For example, coking may occur at locations upstream of the reaction zone, which is the radiant section 40 for this system. To reduce or minimize coking, a catalytic material may be applied upstream of the reaction zone. As a specific example, a structural member may have at least one surface (e.g., at least one surface within the interior (in contact with the hydrocarbon stream) of the separator vessel 5, of the tube banks 2, 6 and 23, of the centrifugal separator 38, of the lines 12, 13, 24 and/or 30, of the phase control valve 36 and of the spargers 4 and 8) having a catalytic material that is disposed over the at least a portion of its surface. This catalytic material may promote the reaction of H_2 and/or oxidant with coke and/or coke precursors at temperatures greater than 150°C, greater than 200°C and/or greater than 250°C.

[0065] As an example, a catalytic material may be utilized in process conditions that reduce coking within the system, extend hydrocarbon processing operations and increase feed flexibility. As an example, the separator vessel 5, condenser 38, lines 13 and 24 and tube bank 23 may include a catalytic material on at least a portion of the surfaces within these structural members. By including the catalytic material, the separator vessel 5 may be operated at process conditions that without the catalytic material would produce more coke (e.g., visbreaking conditions prior to steam cracking in the reaction zone). These process conditions may maximize conversion of resid to lower boiling fractions by increasing the temperatures earlier in the process to promote incipient thermal cracking, which may maximize the portion of the hydrocarbon stream that is vaporized in the separator vessel 5. The process conditions may involve initiating incipient thermal cracking in the tube banks and/or separator vessel 5, and may include temperatures greater than or equal to 371°C, greater than or equal to 399°C, greater than or equal to 415°C and at sufficient partial pressure. The pressure may include 50 psig to 200 psig. These process conditions may maximize conversion of resid to lower boiling fractions, such as resid fractions having

boiling points of up to and in excess of 593°C (593°C$^+$) fractions, and even a portion of the resid fractions up to 760°C.

[0066] The process conditions are performed under an oxidizing or reducing environment as part of the process. That is, upstream of the reaction zone, the different fluids added to the hydrocarbon stream may be managed to control the environment that may promote the conversion of coke and coke precursors via kinetic pathways for removal of the coke and/or coke precursors. In the reducing environment, catalytic material is active to gasify the coke and/or coke precursors. This reducing environment may involve the addition of a hydrogen (H_2) containing stream. Also, for an oxidizing environment, the catalytic material is active to oxidize the coke and/or coke precursors. This oxidizing environment may involve the addition of an oxidant containing stream, such as H_2O, CO_2, O_2, and mixtures thereof.

[0067] Accordingly, with the catalytic material, various stages of feed pretreatment may operate at higher temperatures with reduced coking as opposed to conventional practices, which may provide more of the hydrocarbon feed to the reaction zone and still maintaining or reducing the coking of the upstream equipment surfaces. For instance, the hydrocarbon stream may be heated to temperatures between about 260°C and 360°C in the first tube bank 2, while the stream may be heated in the second tube bank to temperatures between 460°C and 650°C, which is also the temperature utilized in the separator vessel 5. At the separator vessel 5, a hydrogen (H_2) containing stream may be added to the hydrocarbon stream in a hydrogen (H_2) to carbon of greater than 0.1 mole%, 1 mole% or even 5 mole%. Alternatively, steam may be added to the hydrocarbon stream in an amount greater than 1.0 mole%, greater than 20.0 mole%, or even greater than 50.0 mole%. The vapor phase from the separator vessel 5 is further heated in fourth or lower convection section tube bank 23 to temperatures between 620°C to 705°C, while the tubes of the radiant section 40 may further expose the vapor phase to temperatures between 650°C and 1000°C. Further, the temperature of the recycled stream via line 30 may be at temperatures between 360°C to 415°C.

[0068] Further, in addition to the catalytic material upstream of the reaction zone, a catalytic material may be utilized within the reaction zone for certain process conditions. That is, the catalytic material may be utilized on the interior surface of the tubes within the radiant section 40. In the reaction zone, the hydrogen (H_2) containing stream or oxidant containing stream may be added upstream or prior to the radiant zone to provide the proper environment for the catalytic material. In particular, a hydrogen containing stream may be useful to provide that the environment is a reducing environment. The reducing environment

may be beneficial to minimize the undesirable byproducts, such as CO and CO_2, which may result in an oxidizing environment. Regardless, the use of the catalytic material may reduce coking to enhance operations by extending the time that the units may be utilized for hydrocarbon processing operations without having to be interrupted to perform decoking operations.

[0069] Moreover, the catalytic material may be used at downstream locations from the reaction zone. As an example, the catalytic material may be utilized on the interior surface of the lines 41 and 43 along with the interior surfaces the transfer-line exchanger 42. At these downstream locations, a hydrogen (H_2) containing stream or oxidant containing stream may also be added to the reactor product or hydrocarbon stream downstream of the reaction zone and upstream equipment having the catalytic material to provide the proper environment for the catalytic material. The catalytic material may be utilized to reduce the coking resulting from the cooling of the stream, as some molecules begin to condense (e.g., the "dew point"). If this deposition occurs on the internal surface of equipment at these downstream locations, the catalytic material may be utilized to inhibit or reduce coking. Regardless, the use of the catalytic material may reduce coking to enhance operations by extending the time that the equipment may be utilized without having to be interrupted to perform decoking operations.

[0070] Furthermore, in addition to the hydrocarbon processing operations, the catalytic material may be used to enhance decoking operations as well. During decoking operations, air and/or steam is typically provided to the system to burn off any coke deposits. To enhance this decoking operation, it may be beneficial to include a catalytic material on the surface of structural members, similar to those discussed above, which may have coke deposits. The catalytic material may be an oxidation catalyst, which may be rendered catalytically active at process conditions, to promote the reaction of coke and/or coke precursors with the oxidants at temperatures greater than 150°C, greater than 200°C and/or greater than 250°C. The coke at or near the surface may react in the presence of the catalytic material to convert at least a portion of the coke to vapor products, which may be removed from the system. Alternatively, the catalytic material may be a hydrogenation catalyst, which may be rendered catalytically active at process conditions, to promote the reaction of coke with hydrogen (H_2) at temperatures greater than 150°C, greater than 200°C or greater than 250°C. Again, this may involve exposing the coke and catalytic material to a hydrogen (H_2) stream, as noted above.

[0071] Another suitable pyrolysis system, which can benefit from the present techniques, is a regenerative reverse flow reactor system. A regenerative reverse flow reactor system may be used for the manufacture of acetylene from a hydrocarbon feed, such as methane. Fig. 3 illustrates a regenerative reverse flow reactor system 200 having a regenerative reverse flow reactor 202, a separator vessel 223, and two heat exchangers 219 and 229. The regenerative reverse flow reactor 202 has reactor beds 204 and 206 along with one or more injection components 213, 215 and 225, one or more removal components 217 and 227 and one or more lines 212, 214, 218, 220, 222, 224, 228 and 230 providing fluid flow paths through the system. These components manage the flow of various streams (e.g., reactor feeds, combustion feeds, combustion products and reaction products) through the system. Further, the separator vessel 223 and heat exchangers 219 and 229, which may be similar to the transfer line exchanger 42 and separator vessel 5 of Fig. 2.

[0072] The regenerative reverse flow reactor 202 may include any suitable regenerative reverse flow reactor, such as U.S. Published Patent Application No. 2007/0191664 as an example. The reactor beds 204 and 206 are effective in storing and transferring heat to carrying out chemical reactions and to produce products, such as C_{2+} unsaturates (e.g., ethylene and acetylene). These beds 204 and 206 may include glass or ceramic beads or spheres, metal beads or spheres, ceramic (including alumina, zirconia and/or yttria) or metal honeycomb materials, ceramic tubes, extruded monoliths, and the like, provided they are competent to maintain integrity, functionality, and withstand long term exposure to temperatures in excess of 1200°C, preferably in excess of 1500°C, more preferably in excess of 1700°C, and even more preferably in excess of 2000°C within reaction zone 208. The reactor bed(s) 204 and 206 may provide separate channels for the combustion feeds, such as a fuel stream and a combustion oxidant stream, to isolate the streams until they are combined within the reaction zone 208. The combustion oxidant stream may include stream or CO_2, or may be a separate stream, which may include air, but has to include oxygen (O_2). In this manner, the temperature within the reactor may be managed to provide a reaction zone 208 that is the location where the highest temperatures are present.

[0073] The injection components 213, 215 and 225 and removal components 217 and 227 may include one or more valves, reactor heads, manifolds, spargers, tubes and manifolds and other components. Specifically, the injection components 213, 215 and 225 may include injection valves and an injection manifold for each of the different feeds being provided to the reactor 202. Similarly, the removal components 217 and 227 may include one or more

removal valves and removal manifolds. These injection and removal components may be made of a suitable material to provide a structural member, which may be have a catalytic material on the surface of the structural member.

[0074] To operate, the regenerative reverse flow reactor 202 may involve different stages that follow a specific sequence to form a cycle. In particular, the cycle may include a pyrolysis stage and combustion stage. The combustion stage begins with the injection combustion streams, such as a fuel via line 212 and fuel injection manifold 213 and an oxidant via line 214 and oxidant injection manifold 215. The combustion streams may be provided to an end of the second reactor bed 206, passed through the second reactor bed 206 to the reaction zone 208. The combustions streams may exothermically react in the reaction zone 208, which may include a portion of the reactor beds, to heat at least a portion of the reactor bed 204 and at least a portion of reactor bed 206, and are passed to the combustion removal line 216 via the combustion removal component 217 at an end of the reactor bed 204. Based on the flow of the combustion stream, the temperature gradient may reach a peak in the reaction zone 208 near and in a portion of the first reactor bed 204, as the combustion products move across the reactor bed 204 in the direction toward the combustion removal components 217. The fuel and oxidant may be maintained as separate streams to further control the location of the exothermic reaction to the reaction zone 208. Regardless, the combustion products that include CO, CO_2 and/or H_2O may be removed via the removal components 217.

[0075] The pyrolysis stage begins with the injection the hydrocarbon stream, such as methane, natural gas or other suitable reactor feed, via line 224 and feed injection components 225 at the first end of the first reactor bed 204. The hydrocarbon stream passes through the first reactor bed 204 and reacts endothermically from the heat stored in the reactor bed 204. The reactor products may include the reacted products, such as acetylene and/or ethylene, and unreacted hydrocarbons in the stream, which are subsequently cooled as they pass through second reactor bed 206 to the product removal line 228 via the product removal component 227.

[0076] To manage the different streams provided to and removed from the reactor 202, various equipment, such as heat exchangers 219 and 229 and a separator vessel 223, may be utilized as part of this process. The combustion products that include CO, CO_2 and/or H_2O may be removed via the removal components 217 and provided to the combustion heat exchanger 219 to recovery heat from the combustion products. That is, the combustion

products may be cooled by passing water or the hydrocarbon stream at a lower temperature on the utility side of the heat exchanger. Similarly, the hydrocarbon stream may be provided via line 222 to the separator vessel 223 that separates a bottoms product from the hydrocarbon stream (e.g., reactor feed, which may be the vapor phase from the separator vessel 223). The bottoms product may be further processed into fuel or other products, while the remaining hydrocarbon stream may be provided directly to the feed injection component 225 or pass through the heat exchanger 219 to heat the reactor feed prior to the feed injection component 225. The remaining hydrocarbon stream may be provided alone, combined with an oxidant stream or hydrogen containing stream to form the reactor feed. For the reactor product, it may include C_2 unsaturates, may be removed via the product removal components 227, and may be provided to the product heat exchanger 229 to recovery heat from the reactor products. That is, the reactor products may be cooled by passing water, fuel or oxidant at a lower temperature on the utility side of the heat exchanger 229.

[0077] To operate, the various stages for the hydrocarbon processing operations may involve different process conditions for the respective stream (e.g., heat the respective streams to different temperatures). For instance, the hydrocarbon stream may be heated prior to the separator vessel 223 to temperatures in the range of 100°C and 500°C. The initial heating may be performed in combustion heat exchanger 219, which utilizes the heat from the combustion products to heat the hydrocarbon stream, or may be performed in another unit, such as a furnace or boiler. Also, the process may involve passing the vapor product from the separator vessel 223 through the combustion heat exchanger 219 to further heat the vapor phase from the combustion products prior to the reactor 202. Regardless, the heated hydrocarbon stream (e.g., the reactor feed) is provided to the reactor and passes through the feed injection component 225 and first reactor bed 204. In the reaction zone 208, the hydrocarbons are exposed to temperatures in the range of 1200°C to 2200°C, in the range of 1500 °C to 2000°C, or in the range of 1600°C to 1800°C, which convert hydrocarbons in the hydrocarbon stream into the reactor product. Then, the reactor product is passed through the second reactor bed 206 to the product removal component 227 and the heat exchanger 229. The reactor product may be provided to the heat exchanger 229 at temperatures in the range of 250°C to 500°C, and may be cooled to temperatures in the range of 150°C to 400°C.

[0078] Similar to the steam cracking system above, the formation of coke and/or coke precursors may be a problem within this system. Further, this process has some additional aspects that should be considered. In particular, the process conditions in the reactor 202

include both oxidizing and reducing environments, which are subject to the different stages in the cycle. That is, at least a portion of the components within the reactor 202 are exposed to both environments, while outside the reactor's interior region (e.g., within the injection and removal components and subsequent lines and equipment), the surfaces of the components may only be exposed to one environment during normal operations, which is similar to the steam cracking system, and may be exposed to an oxidizing environment during decoking operations. Accordingly, for this system different fluids may be added to the hydrocarbon stream, fuel stream and/or combustion oxidant stream to control the environment in a manner that promotes the conversion of coke and coke precursors via kinetic pathways for removal of the coke and/or coke precursors. Further, the catalytic material may be utilized at certain locations on the reactor beds 204 and 206, which are not exposed to temperatures greater than 600°C, greater than 750°C or even greater than 900°C. That is, the catalytic material may be utilized on the ends of the reactor beds 204 and 206 (e.g., portions of the reactor beds 204 and 206 that are not within the reaction zone 208 or exposed to higher temperatures that may damage the catalytic material).

[0079] Accordingly, a catalytic material may be utilized in process conditions that reduce coking within the system, extend hydrocarbon processing operations and increase feed flexibility. For example, coking may occur at locations upstream of the reaction zone 208 for the hydrocarbon stream. To reduce or minimize coking, a catalytic material may be applied upstream of the reaction zone. As a specific example, a structural member having at least one surface (e.g., at least one surface within the interior (in contact with the hydrocarbon stream) of the separator vessel 223, of the combustion heat exchanger 219, of the feed injection components or of portions of the combustion removal components 225, 217, or portions thereof, such as poppet valve heads (not shown), within the reactor 202, of the reactor bed 204 and/or of the lines 222, 224 and/or others (not shown)) having a catalytic material over the at least one surface. This catalytic material may be rendered catalytically active for the reaction with coke and/or coke precursors at temperatures greater than 150°C, greater than 200°C and/or greater than 250°C. The catalytic material may be utilized on the reactor bed 204 near the feed injection end, which is not exposed to temperatures that may damage the catalytic material, as noted above.

[0080] Similar to the discussion above, the catalytic material may form a layer on the surfaces within these structural members. By including the catalytic material, the separator vessel 223 may be operated at process conditions that produce more coke (e.g., visbreaking

conditions). These process conditions may maximize conversion of resid to lower boiling fractions by increasing the temperatures earlier in the process to promote incipient thermal cracking, which may maximize the portion of the hydrocarbon stream that is vaporized in the separator vessel 223. The process conditions may involve initiating incipient thermal cracking in the heat exchanger 219 and/or separator vessel 223, and may include temperatures greater than or equal to 371°C, greater than or equal to 399°C, greater than or equal to 415°C and at sufficient process pressure to enable flow to the next process step.

[0081] As noted above, the process environment may be adjusted to further enhance the process. In particular, a hydrogen (H_2) containing stream or oxidant stream may be added to the separator 223 or upstream of the separator 223 to provide a specific environment. That is, hydrogen (H_2) may be added to the hydrocarbon stream to provide a reducing environment or alternatively, steam may be added to the hydrocarbon stream to provide an oxidizing environment.

[0082] While the catalytic material may not be utilized within the reaction zone 208 because of the higher temperatures, a catalytic material may be utilized downstream of the reaction zone 208 within the reactor 202 and on surfaces downstream of the reactor 202. As a specific example, a structural member may have at least one surface (e.g., at least one surface within the interior (in contact with the reactor products) of the injection components 213 and/or 215 within the reactor 202 (such as, poppet valve heads), of the heat exchanger 229, portion of the injection components 225, of portions of the combustion removal components 217 within the reactor 202 (poppet valve heads), of the reactor bed 204 and/or of the lines 228 and/or 230) having a catalytic material on at least one surface. As noted above, these downstream locations may also include the addition of a hydrogen (H_2) containing stream or oxidant containing stream to the reactor product or hydrocarbon stream downstream of the reaction zone 208 and upstream equipment having the catalytic material to provide the proper environment for the catalytic material. The catalytic material may be utilized to reduce the coking resulting from the cooling of the stream, as some molecules begin to condense (e.g., the "dew point"). Regardless, the use of the catalytic material may reduce coking (e.g., to prevent oligomerization or polymerization of those materials and subsequent deposition as coke) to enhance operations by extending the time that the equipment may be utilized without having to be interrupted to perform decoking operations.

[0083] With regard to the combustion stage of the cycle, the fuel stream, combustion oxidant stream and combustion products may also be utilized to reduce coking and enhance

the process. For example, coking may occur at locations upstream of the reaction zone 208 for the fuel stream, while the combustion oxidant stream is expected to remove coke in the portions of the reactor bed 206 that the combustion oxidant stream flows through. Accordingly, to reduce or minimize coking, a catalytic material may be applied upstream of the reaction zone 208 for these streams. As a specific example, a structural member may have at least one surface (e.g., at least one surface within the interior (in contact with the fuel or combustion oxidant streams) of the injection components 213 and 215, of the heat exchanger 229 which is exposed to the combustion oxidant or fuel stream, of a portion of the removal component 227 that are exposed to the streams (such as, the poppet valve heads), of the reactor bed 206 and/or of the lines 212 and/or 214) having a catalytic material on the at least one surface. This catalytic material is rendered catalytically active for the reaction with coke and/or coke precursors at temperatures greater than 150°C, greater than 200°C and/or greater than 250°C, but should not be exposed to certain temperatures, as noted above.

[0084] Similar to the discussion above, the catalytic material may be used on surfaces within these structural members that are utilized to provide the fuel stream to the reactor. By including the catalytic material, the fuel stream to the reactor 202 may be provided at process conditions that may produce coke. That is, the fuel stream or combustion oxidant stream may recover heat from the reactor products in the heat exchanger 229. By providing the fuel stream at these higher temperatures, the reactor 202 may be managed to reduce the temperature swing within the reactor 202, which reduces fatigue on components within the reactor, enhances the energy efficiency by reducing the amount of heat to be generated, and enhance efficiency by recovering heat from the different streams.

[0085] Also, the process environment may be adjusted to further enhance the process. In particular, a hydrogen (H_2) containing stream or oxidant stream may be added to the separator vessel 223 or upstream of the separator vessel 223 to provide a specific environment. That is, hydrogen (H_2) may be added to the hydrocarbon stream to provide a reducing environment or alternatively, an oxidant, such as steam, may be added to the hydrocarbon stream to provide an oxidizing environment. The use of these streams operates similar to the discussion above.

[0086] While the catalytic material may not be utilized within the reaction zone 208 because of the higher temperatures, as noted above, a catalytic material may be utilized downstream of the reaction zone 208 within the reactor 202 and on surfaces downstream of the reactor 202. As a specific example, a structural member may have at least one surface

(e.g., at least one surface within the interior (in contact with the combustion products) of the injection components 225 within the reactor 202 (such as, poppet valve heads), of the heat exchanger 219, portion of the removal components 217, of the reactor bed 204 and/or of the lines 218 and/or 220) having a catalytic material on the at least one surface. As noted above, these downstream locations may also include the addition of a hydrogen (H_2) containing stream or oxidant containing stream to the combustion product downstream of the reaction zone 208 and upstream equipment having the catalytic material to provide the proper environment for the catalytic material.

[0087] Further, as yet another embodiment, the process may be conducted in a pyrolysis system that includes a pulsed compression reactor in the pretreatment stages for a pyrolysis unit. In this embodiment 300, a preheater 302, a pulsed compression reactor 304, a wash drum 306, a high pressure separator 308 and pyrolysis unit 310 are coupled together via lines 320, 322, 324, 326, 330, 332, 334, 336 and 338. This system may utilize a catalytic material to enhance the processing of a hydrocarbon stream in a manner similar to the discussion above of the steam cracking system of Fig. 2 or regenerative reverse flow reactor system of Fig. 3. The embodiment is explained in further detail below.

[0088] To begin, a hydrocarbon stream in line 320 is combined with a hydrogen containing stream via line 322, and optionally with steam via line 324, a catalyst stream via line 326, and/or a recycle stream (not shown); and sent to a preheater 302. The mixture of lines 320, 322, 324 and 326 are initially provided to a pre-heater 302 to heat to a temperature sufficient to vaporize at least a portion of the mixture. The preheater may include a heat exchanger, boiler or other suitable device. Then, the heated mixture is provided to the pulsed compression reactor 304 via line 330. The pulsed compression reactor 304 may be any suitable pulsed compression reactor, such as the pulsed compression reactor disclosed in U.S. Patent Serial No. 12/689,154, incorporated by reference herein in its entirety. The pulsed compression reactor 304, which comprises a free piston enclosed within a double-ended cylinder having an inlet port and an outlet port. The piston is free to reciprocate between limiting positions so as to form compression chambers at either end of the cylinder between the end of the free piston and the internal surface of the cylinder end, which is either coated or impregnated with the catalytic materials of the present techniques.

[0089] In the pulsed compression reactor 304, the mixture flows across the cylinder in which the free piston, dividing the cylinder into two compression-reaction chambers, reciprocates with a very high frequency, such as up to 400 Hz, compressing the mixture in

lower and upper chambers. The rapid compression of the mixture in each chamber results in its heating to sufficiently high temperatures and pressures to drive chemical reactions. Advantageously, when the chemical reaction is exothermic, the resulting expansion of the reactants acts to force the piston in the opposite direction to compress the reactants in the opposite compression chamber. A reaction product exits outlet port via line 332 to wash drum 306.

[0090] In a preferred embodiment, catalytically active metals/compounds for hydrogenation, such as Mo, Ni, Co, V, Fe, Cu and/or compounds thereof, and combinations thereof may be added as a mobile catalyst to the distillate feed via stream 326, and/or recycled via stream, to enhance the hydrogenation reactions which occur. A mobile catalyst may comprise: (i) a vapor phase species, (ii) a liquid phase species; (iii) a material dissolved in a hydrocarbon; and/or (iv) solid particles of sufficiently small size to be entrained in the hydrocarbon. In a particularly preferred embodiment, the hydrogenation catalysts are deposited on a carbonaceous solid, such as soot formed during the process, which aids in hydrogen transfer. In an alternative embodiment, the hydrogenation catalyst may be a stationary catalyst which is incorporated within combustion chambers.

[0091] Due to the short residence times and rapid decompression inherent in the compression reactor 304, the stream leaving the reactor 304 through line 332 are rapidly quenched, avoiding undesirable chemical recombinations, such as oligomerization or polymerization, of the reaction products. The wash drum 306 acts to remove catalyst/soot and uncracked bottoms as a liquid stream from the vaporized stream, and recycle those liquid by-products via line (not shown) to the beginning of the process. A portion of the bottoms from the wash drum 306 may be purged to remove and recover excess soot and metals (not shown). The soot and metals may be separated or concentrated from the bulk of the bottoms from the wash tower by filtration or centrifugation.

[0092] The washed stream are passed through line 334, optionally cooled, and sent into a high pressure separator 308 to separate remaining hydrogen-containing gas (not shown) for potential recycle to the system, or for other refinery uses, and the upgraded liquid hydrocarbon via line 336, (e.g., the hydroprocessed product), may be sent downstream to a pyrolysis unit 310, such as a steam cracker or regenerative reverse flow reactor. In one embodiment, the upgraded liquid hydrocarbon is sent to a vapor/liquid separator or separator 310, wherein at least a portion of the separated hydrocarbon vapors via line 338 are

forwarded to a steam cracker for further cracking, and the separated liquid bottoms 340 may be recycled to wash drum 306.

[0093] According to the present embodiment, liquid hydrocarbon feeds, even ones containing resid, can be hydroprocessed in a pulsed compression reactor as a pretreatment for the pyrolysis unit 310. Suitable liquid hydrocarbon feeds may include, but are not limited to vacuum tower bottoms, resid, fuel oil, steam cracking separator bottoms (e.g., flash drum bottoms prior to the cracking the feed), atmospheric tower bottoms, steam cracker tar, whole crude oil, coker products, and/or FCC bottoms.

[0094] The formation of coke and/or coke precursors may be a problem within this system, as noted above with the other systems. For example, coking may occur at locations upstream of the reaction zone, which is within the pyrolysis unit 310. To reduce or minimize coking, a catalytic material may be applied upstream of the reaction zone. As a specific example, a catalytic material may be applied to structural members having at least one surface (e.g., at least one surface within the interior (in contact with the hydrocarbon stream) of the preheater 302, at the top of each end of the cylinder in a pulsed compression reactor 304 and/or on the piston within the pulsed compression reactor 304, within high pressure separator 308 and/or within the of the lines 320, 322, 330, 332, 334 and/or 336) having a catalytic material on the at least one surface. This catalytic material is rendered catalytically active for the reaction with coke and/or coke precursors at temperatures greater than 150°C, greater than 200°C and/or greater than 250°C.

[0095] Beneficially, the catalytic material may be utilized in process conditions that reduce coking within the system, extend hydrocarbon processing operations and increase feed flexibility, as noted above with the other systems. As an example, the preheater 302, pulsed compression reactor 304 and lines 320, 330 and 332 may have a catalytic material on at least one surface within the interior of these structural members in contact with the hydrocarbon stream. By including the catalytic material, the preheater 302 and pulsed compression reactor 304 may be operated at process conditions that produce more coke (e.g., visbreaking conditions prior to the cracking in the reaction zone). This may operate similar to the steam cracking conditions, which include process conditions to initiate incipient thermal cracking. Specifically, it may involve temperatures greater than or equal to 371°C, greater than or equal to 399°C, greater than or equal to 415°C and at sufficient partial pressure in the preheater 302 to maximize conversion of resid to lower boiling fractions, such as resid fractions having

boiling points of up to and in excess of 593°C (593°C$^+$) fractions, and even a portion of the resid fractions up to 760°C.

[0096] Further, as noted above, the environment for this process may include an oxidizing or reducing environment. That is, upstream of the reaction zone, the different fluids added to the hydrocarbon stream to control the environment and promote the conversion of coke and coke precursors via kinetic pathways for removal of the coke and/or coke precursors. Accordingly, with the catalytic material, various stages may operate at higher temperatures with reduced coking as opposed to conventional practices, while providing more of the hydrocarbon feed to the reaction zone and still maintaining or reducing the coking of the upstream equipment surfaces. For instance, the hydrocarbon stream may be heated to temperatures between about between 360°C and 650°C in the preheater 302 and in the pulsed compression reactor 304. At the preheater 302, a hydrogen (H_2) containing stream may be added to the hydrocarbon stream in an amount of greater than 0.1 mole% or greater than 1 mole%, but less that 5 mole% or less than 4 mole% to provide a reducing environment. Alternatively, steam may be added to the hydrocarbon stream to provide an oxidizing environment, as noted above. The mixture from the preheater 302 may be provided to the pulsed compression reactor 304 to convert the hydrocarbons at temperatures between 650°C and 1000°C. Further, the temperature of the wash drum 306 and high pressure separator 308 may be between 100°C and 1000 °C.

[0097] Further, in addition to the catalytic material upstream of the reaction zone, the catalytic material may be utilized within the reaction zone or downstream of the reaction zone, as noted above for the other systems.

[0098] Other embodiments may include other different application of the catalytic material. Likewise, the present techniques may be utilized within a thermal coking system, wherein conversion of a hydrocarbon stream to produce coke, hydrocarbon gases, and light hydrocarbon liquids are conducted. Such systems generally include a thermal coking unit along with pretreatment and recovery units, which may include heat exchangers, preheat furnaces and separator vessels. Regardless, of the specific configuration, the catalytic materials may be disposed on or incorporated into the surfaces upstream and downstream of the thermal coking unit, such as various tubes (e.g., conduits and piping) for carrying vaporized hydrocarbons to and from the thermal coking unit and the other units, as noted above.

[0099] Further still, the present techniques may be utilized for catalytic olefin generation system, wherein conversion of a hydrocarbon stream to produce coke, hydrocarbon gases, and light hydrocarbon liquids are conducted. Such systems generally include a fluid catalytic cracking reactor along with pretreatment and recovery units, which may include heat exchangers, preheat furnaces and separator vessels. Regardless, of the specific configuration, the catalytic materials may be disposed on or incorporated into the surfaces upstream and downstream of the fluid catalytic cracking reactor, such as various conduits and piping for carrying vaporized hydrocarbons to and from the fluid catalytic cracking reactor and the other units, as noted above.

[00100] Moreover, the process of the present techniques may be utilized in catalytic hydrodearomatization processes of naphtha boiling range materials to product aromatic rich streams for motor gasoline and/or chemical feedstocks, wherein the at least one surface in contact with the hydrocarbon feed are inner surfaces of process tubes for feed preheating and/or inter-catalyst stage reheating, wherein lighter hydrocarbons are vaporized and can deposit as coke. Again, these processes and apparatuses for conducting them are well-known in the art.

[00101] In yet another embodiment, the process of the present techniques is conducted within a hydroconversion process of a hydrocarbon feed to reduce sulfur compounds, nitrogen compounds, aromatic compounds, and/or boiling point distribution, and the at least one surface in contact with the hydrocarbon feed are inner surfaces of process tubes for feed preheating, again where lighter hydrocarbons are vaporized and non-volatile components may deposit as coke.

[00102] One or more embodiments may involve the following paragraphs:

1. A method of converting hydrocarbons into C_{2+} unsaturates comprising: providing at least one structural member upstream of a reaction zone at least a portion of an inner surface of such member comprising a catalytic material (which may be rendered catalytically active at process conditions) that promotes the reaction of coke and/or coke precursors with hydrogen (H_2) and/or an oxidant to form vapor products; exposing a hydrocarbon stream that contains coke and/or coke precursors to the catalytic material in the presence of hydrogen and/or an oxidant and reacting at least a portion of the coke and/or coke precursors to form vapor products; and converting at least a portion of the hydrocarbon stream containing the hydrocarbons and the vapor products in the reaction zone to produce a reactor product having C_{2+} unsaturates.

2. The method of paragraph 1, wherein the reaction zone is a radiant section of a steam cracking furnace downstream of a convection section and/or wherein the converting is thermally cracking performed in a steam cracking furnace having the convection section and the radiant section.

3. The method of paragraph 2, wherein the at least one structural member comprises a process tube in the convection section of the steam cracking furnace.

4. The method of any one of paragraphs 2 to 3, wherein the at least one structural member further comprises a separator vessel integrated with the convection section of the steam cracking furnace.

5. The method of any one of paragraphs 2 to 4, wherein the at least one structural member comprises a process tube coupled between a separator vessel and the radiant section of the steam cracking furnace.

6. The method of any one of paragraphs 2 to 5, wherein the separator vessel is a single unit configured to receive the hydrocarbon stream and separate the stream into a vapor portion provided to an overhead line and a bottoms portion provided via a bottoms line.

7. The method of any one of paragraphs 2 to 6, wherein the at least one structural member further comprises one of a chamber of a pulsed compression reactor, a piston of the pulsed compression reactor, a process tube coupled between the pulsed compression reactor and the radiant section of the steam cracking furnace and any combination thereof, wherein the pulsed compression reactor is upstream of the radiant section of the steam cracking furnace.

8. The method of any one of paragraphs 1 to 7, further comprising exposing at least a portion of the reactor product that contains coke and/or coke precursors to at least one structural member downstream of the reaction zone, wherein at least a portion of the surface of such structural member comprises a downstream catalytic material thereon that promotes the reaction of the coke and/or coke precursors with hydrogen and/or an oxidant to form vapor products.

9. The method of paragraph 8, wherein the at least one structural member downstream of the reaction zone is one of a process tube downstream of a radiant section of the steam cracking furnace, a process tube in transfer line exchanger and any combination thereof.

10. The method of any one of paragraphs 1 to 9 comprising exposing at least a portion of the reactor product to at least one structural member in the reaction zone and having at least one surface of a reaction zone catalytic material, wherein the reactor product comprises coke

and/or coke precursors that react in the presence of the reaction zone catalytic material to convert at least a portion of the coke and/or coke precursors to vapor products.

11. The method of paragraph 1, wherein the reaction zone is a portion of a regenerative reverse flow reactor.

12. The method of paragraph 11, wherein the at least one structural member comprises one of a feed injection component upstream of the regenerative reverse flow reactor, a process tube upstream of the regenerative reverse flow reactor, and any combinations thereof.

13. The method of paragraph 11, wherein the at least one structural member comprises a poppet valve, wherein the surface is the portion of the poppet valve continuously exposed to an interior region of the regenerative reverse flow reactor.

14. The method of any one of paragraphs 11 to 13, wherein the at least one structural member further comprises a separator vessel upstream of the regenerative reverse flow reactor.

15. The method of any one of paragraphs 11 to 14, wherein the at least one structural member comprises a process tube coupled between a separator vessel and the regenerative reverse flow reactor.

16. The method of any one of paragraphs 11 to 15, wherein the at least one structural member further comprises a heat exchanger upstream of the regenerative reverse flow reactor.

17. The method of any one of paragraphs 1 and 11 to 16, further comprising exposing at least a portion of the reactor product that contains coke and/or coke precursors to at least one structural member downstream of the reaction zone, wherein at least a portion of the surface of the structural member comprises a downstream catalytic material that promotes the reaction of coke and/or coke precursors with hydrogen and/or oxidant to form vapor products.

18. The method of paragraph 17, wherein the at least one structural member downstream of the reaction zone is one of a process tube downstream of the reaction zone, a removal component, a portion of the reactor bed adjacent to the removal component, a process tube in a transfer line exchanger, and any combination thereof.

19. The method of any one of paragraphs 17 and 18, wherein the at least one structural member downstream of the reaction zone comprises a poppet valve, wherein the surface is the portion of the poppet valve continuously exposed to the interior region of the regenerative reverse flow reactor.

20. The method of any one of the paragraphs 11 to 19, wherein the converting step comprises thermally cracking the hydrocarbon stream by exposure to temperatures in the range of 1200°C to 2200°C in the reaction zone.

21. The method of any one of paragraphs 1 to 20, wherein a hydrocarbon stream contains greater than or equal to 1 wt% non-volatile non-combustibles.

22. The method of any one of paragraphs 1 to 21, wherein hydrogen (H_2) is added to the hydrocarbon stream upstream of the catalytic material in an amount of greater than 0.1 mole percent and less than 5.0 mole percent.

23. The method of any one of paragraphs 1 to 21, wherein hydrogen (H_2) is added in a ratio of hydrogen to carbon (H_2/C) in the range of 0.1 to 5.0 in the hydrocarbon stream.

24. The method of any one of paragraphs 1 to 23, wherein the hydrocarbon stream comprises combustible non-volatiles below 1 wt% of the hydrocarbons in the hydrocarbon stream that is subject to the converting.

25. The method of any one of paragraphs 1 to 24, wherein greater than 75 % of heat for the converting is provided via indirect heat transfer.

26. The method of any one of paragraphs 1 to 25, wherein the catalytic material comprises one or more of the elements from Group IVB-VIIIB and Group IA-IVA and oxides, sulfides, nitrides, carbides intermetallic and/or reduced metal species.

27. The method of any one of paragraphs 1 to 26, wherein the catalytic material is selected to provide a surface net coke deposition rate of less than 0.1 $g/m^2/hr$.

28. The method of any one of paragraphs 1 to 21, wherein oxidant is added to the hydrocarbon stream upstream of the catalytic material in a ratio of oxygen to carbon (O/C) in the range of 0.01 to 0.6.

29. A pyrolysis system comprising: a pyrolysis unit having a reaction zone, wherein the pyrolysis unit is configured to convert hydrocarbons into C_{2+} unsaturates; and at least a portion of a surface of at least one structural member upstream of the reaction zone comprises a catalytic material thereon (which may be rendered catalytically active at process conditions) that promotes the reaction of coke and/or coke precursors with hydrogen (H_2) and/or an oxidant.

30. The pyrolysis system of paragraph 29, wherein the pyrolysis unit is a steam cracking furnace having a convection section and a radiant section.

31. The pyrolysis system of paragraph 30, wherein the at least one structural member upstream of the reaction zone comprises one or more of a process tube in the convection

section of the steam cracking furnace, a separator vessel integrated with the convection section of the steam cracking furnace, a process tube coupled between the separator vessel and the radiant section of the steam cracking furnace, a chamber of a pulsed compression reactor, and a piston of the pulsed compression reactor and any combination thereof, wherein the pulsed compression reactor is upstream of the radiant section of the steam cracking furnace.

32. The pyrolysis system of any one of paragraphs 30 to 31, comprising at least one structural member downstream of the reaction zone and having at least one surface of a downstream catalytic material, wherein the downstream catalytic material is rendered catalytically active to promote the reaction of coke and/or coke precursors with hydrogen (H_2) and/or an oxidant.

33. The pyrolysis system of paragraph 32, wherein the at least one structural member downstream of the reaction zone is one or more of a process tube downstream of a radiant section of the steam cracking furnace, and a process tube in transfer line exchangers.

34. The pyrolysis system of any one of paragraphs 30 to 33, wherein the reaction zone comprises a radiant section tube having at least one surface of a reaction zone catalytic material, wherein the reaction zone catalytic material is rendered catalytically active to promote the reaction of coke and/or coke precursors with hydrogen (H_2) and/or an oxidant.

35. The pyrolysis system of paragraph 29, wherein the pyrolysis unit is a regenerative reactor or a regenerative reverse flow reactor.

36. The pyrolysis system of paragraph 35, wherein the at least one structural member upstream of the reaction zone and comprises one or more of a feed injection component upstream of the regenerative reverse flow reactor, a process tube upstream of the regenerative reverse flow reactor, a poppet valve, wherein the surface is the portion of the poppet valve continuously exposed to the interior region of the regenerative reverse flow reactor, a separator vessel upstream of the regenerative reverse flow reactor, a process tube coupled between the separator vessel and the regenerative reverse flow reactor, and a heat exchanger upstream of the regenerative reverse flow reactor.

37. The pyrolysis system of any one of paragraphs 29, 35 and 36 comprising at least one structural member downstream of the reaction zone, wherein the at least one structural member has a downstream catalytic material that reacts coke and/or coke precursors in the presence of the downstream catalytic material to convert at least a portion of the coke and/or coke precursors to vapor products.

38. The pyrolysis system of paragraph 37, wherein the at least one structural member downstream of the reaction zone is one or more of a process tube, a removal component, a portion of the reactor bed adjacent the removal component, a process tube in a transfer line exchanger, and a poppet valve, wherein the surface is the portion of the poppet valve continuously exposed to the interior region of the regenerative reverse flow reactor.

39. The pyrolysis system of any one of paragraphs 29 to 38, wherein greater than 75 % of the heat for the converting is provided via indirect heat transfer.

40. The pyrolysis system of any one of paragraphs 29 to 39, wherein the catalytic material comprises one or more elements from Group IVB-VIIIB and Group IA-IVA and oxides, sulfides, nitrides, carbides intermetallic and/or reduced metal species thereof.

41. The pyrolysis system of any one of paragraphs 29 to 40, wherein the catalytic material is selected to provide a surface net coke deposition rate of less than 0.1 $g/m^2/hr$.

42. A method of converting hydrocarbons into C_{2+} unsaturates comprising:

converting the hydrocarbon stream in a reaction zone of a regenerative reverse flow reactor to produce a reactor product comprising C_{2+} unsaturates and hydrogen (H_2);

exposing at least a portion of the reactor product to at least one structural member having at least a portion of the surface of the at least one structural member having the catalytic material thereon (which may be rendered catalytically active at process conditions), wherein the catalytic material promotes the reaction of coke and/or coke precursors with hydrogen (H_2) and/or an oxidant at temperatures greater than 150°C; and

reacting in the presence of the catalytic material at least a portion of the coke and/or coke precursors with the hydrogen (H_2) and/or oxidant to convert the coke and/or coke precursors to vapor products.

43. The method of paragraph 42, wherein the at least one structural member is one of a process tube downstream of the reaction zone, a removal component, a portion of the reactor bed adjacent the removal component, a process tube in a transfer line exchanger, and any combination thereof.

44. The method of any one of paragraphs 42 and 43, wherein the at least one structural member comprises a poppet valve, wherein the surface is the portion of the poppet valve continuously exposed to the interior region of the regenerative reverse flow reactor.

45. The method of any one of the paragraphs 42 to 44, wherein the converting comprises exposing the hydrocarbon stream to temperatures in the range of 1200°C to 2200°C.

46. The method of any one of paragraphs 42 to 45, wherein hydrogen (H_2) is added to the reactor product upstream of the catalytic material in an amount of greater than 0.1 mole percent and less than 5.0 mole percent.

47. The method of any one of paragraphs 42 to 46, wherein hydrogen (H_2) is added in a ratio of hydrogen to carbon (H_2/C) in the range of 0.1 to 5.0 in the hydrocarbon stream.

48. The method of any one of paragraphs 42 to 47, wherein greater than 75 % of the heat for the converting is provided via indirect heat transfer.

49. The method of any one of paragraphs 42 to 48, wherein the catalytic material comprises one or more elements from Group IVB-VIIIB and Group IA-IVA and oxides, sulfides, nitrides, carbides intermetallic and/or reduced metal species thereof.

50. The method of any one of paragraphs 42 to 49, wherein the catalytic material is selected to provide a surface net coke deposition rate of less than 0.1 g/m^2/hr.

51. The method of any one of paragraphs 42 to 50, wherein oxidant is added to the reactor product upstream of the catalytic material in a ratio of oxygen to carbon (O/C) in the range of 0.01 to 0.6.

52. A pyrolysis system comprising:

a regenerative reverse flow reactor having a reaction zone, wherein the regenerative reverse flow reactor is configured to convert hydrocarbons into C_{2+} unsaturates; and

at least one structural member downstream of the reaction zone having at least one surface of a catalytic material, wherein the catalytic material promotes the reaction of coke and/or coke precursors with hydrogen (H_2) and/or an oxidant to form vapor products.

53. The pyrolysis system of paragraph 52, wherein the at least one structural member is one or more of a process tube downstream of the reaction zone, a removal component, a portion of the reactor bed adjacent the removal component, a process tube in a transfer line exchanger, a poppet valve, wherein the surface is the portion of the poppet valve continuously exposed to the interior region of the regenerative reverse flow reactor.

54. The pyrolysis system of any one of paragraphs 52 to 53, wherein the catalytic material comprises one or more elements from Group IVB-VIIIB and Group IA-IVA and oxides, sulfides, nitrides, carbides intermetallic and/or reduced metal species thereof.

55. The pyrolysis system of any one of paragraphs 52 to 54, wherein the catalytic material is selected to provide a surface net coke deposition rate of less than 0.1 g/m^2/hr.

[00103] One or more other embodiments may involve the following paragraphs:

1A. A method of converting hydrocarbons into C_{2+} unsaturates comprising:

converting a first hydrocarbon stream into a reactor product comprising C_{2+} unsaturates and coke in a reaction zone of a regenerative reverse flow reactor having a reactor bed and at least one structural member adjacent to an end of the reactor bed, wherein the at least one structural member comprises one or more of a removal component and a injection component;

removing a first portion of the reactor product comprising C_{2+} unsaturates and a portion of the coke from the reaction zone;

exposing an oxidant stream to the at least one structural member having at least a portion of a surface with a catalytic material thereon that promotes the reaction of coke with the oxidant stream;

reacting the oxidant stream with the second portion of the reactor products comprising coke in the presence of the catalytic material to convert at least a portion of the coke to vapor products;

exothermically reacting the remaining oxidant stream with a fuel stream in the reaction zone to produce a combustion product; and

removing the combustion product prior to the providing a second hydrocarbon stream to the reaction zone.

2A. The method of paragraph 1A, wherein the at least one structural member comprises a poppet valve, wherein the surface is the portion of the poppet valve continuously exposed to an interior region of the regenerative reverse flow reactor.

3A. The method of any one of paragraphs 1A to 2A, further comprising disposing a catalytic material on at least a portion of a surface of the reactor bed adjacent the at least one structural member, wherein the catalytic material promotes the reaction of coke with the oxidant stream at temperatures less than 600°C.

4A. The method of any one of the paragraphs 1A to 3A, wherein the converting comprises exposing the hydrocarbon stream to temperatures in the range of 1400°C to 2200°C.

5A. The method of any one of paragraphs 1A to 4A, wherein the first hydrocarbon stream comprises combustible non-volatiles below 1 wt% of the hydrocarbons in the first hydrocarbon stream that are subject to the converting.

6A. The method of any one of paragraphs 1A to 5A, wherein greater than 75 % of heat for the converting is provided via indirect heat transfer.

7A. The method of any one of paragraphs 1A to 6A, wherein the catalytic material comprises one or more of the elements from Group IVB-VIIIB and Group IA-IVA and oxides, sulfides, nitrides, carbides intermetallic and/or reduced metal species.

8A. The method of any one of paragraphs 1A to 7A, wherein the catalytic material is selected to provide a surface net coke deposition rate of less than 0.1 $g/m^2/hr$.

9A. A method of converting hydrocarbons into C_{2+} unsaturates comprising: converting a first hydrocarbon stream into a reactor product comprising C_{2+} unsaturates and coke in a reaction zone of a regenerative reverse flow reactor having a reactor bed and at least one structural member adjacent to an end of the reactor bed, wherein the at least one structural member comprises one or more of a removal component and an injection component; removing a first portion of the reactor product comprising C_{2+} unsaturates and a portion of the coke from the reaction zone; exothermically reacting an oxidant stream with a fuel stream in the reaction zone to produce a combustion product; exposing the combustion product to the at least one structural member having at least a portion of a surface with a catalytic material, wherein the catalytic material promotes the reaction of coke with the combustion product; reacting the combustion product with the second portion of the reactor products comprising coke in the presence of the catalytic material to convert at least a portion of the coke to vapor product; and removing the combustion product and at least a portion of the vapor product prior to the providing a second hydrocarbon stream to the reaction zone.

10A. The method of paragraph 9A, wherein the at least one structural member comprises one of a feed injection component downstream of the reaction zone for the combustion product.

11A. The method of paragraph 9A, wherein the at least one structural member comprises a poppet valve, wherein the surface is the portion of the poppet valve continuously exposed to an interior region of the regenerative reverse flow reactor.

12A. The method of any one of paragraphs 9A to 11A, wherein the at least one structural member comprises a portion of the reactor bed adjacent to a combustion removal component downstream of the reaction zone for the combustion products.

13A. The method of any one of paragraphs 9A to 12A, wherein the at least one structural member comprises a process tube coupled between combustion removal components and a heat exchanger downstream of the regenerative reverse flow reactor for the combustion products.

14A. The method of any one of paragraphs 9A to 13A, wherein the at least one structural member comprises a heat exchanger downstream of the regenerative reverse flow reactor for the combustion products.

15A. The method of any one of the paragraphs 9A to 14A, wherein the converting comprises exposing the hydrocarbon stream to temperatures in the range of 1200°C to 2200°C.

16A. The method of any one of paragraphs 9A to 15A, wherein the first hydrocarbon stream comprises combustible non-volatiles below 1 wt% of the hydrocarbons in the hydrocarbon stream that are subject to the converting.

17A. The method of any one of paragraphs 9A to 16A, wherein greater than 75 % of heat for the converting is provided via indirect heat transfer.

18A. The method of any one of paragraphs 9A to 17A, wherein the catalytic material comprises one or more of the elements from Group IVB-VIIIB and Group IA-IVA and oxides, sulfides, nitrides, carbides intermetallic and/or reduced metal species.

19A. The method of any one of paragraphs 9A to 18A, wherein the catalytic material is selected to provide a surface net coke deposition rate is less than 0.1 $g/m^2/hr$.

20A. A pyrolysis system comprising: a regenerative reverse flow reactor having a reaction zone, wherein the regenerative reverse flow reactor is configured to convert hydrocarbons into C_{2+} unsaturates; and at least a portion of a surface of at least one structural member having a catalytic material, wherein the catalytic material promotes the reaction of coke and/or coke precursors with an oxidant.

21A. The pyrolysis system of paragraph 20A, wherein the at least one structural member is one or more of a process tube downstream of the reaction zone, a combustion removal component downstream of the reaction zone, a portion of the reactor bed adjacent the combustion removal component, a process tube in a transfer line exchanger downstream of the reaction zone, and a poppet valve, wherein the surface of the poppet valve is the portion of the poppet valve that is continuously exposed to the interior region of the regenerative reverse flow reactor.

22A. The pyrolysis system of paragraph 20A, wherein the at least one structural member is one or more of a product removal component upstream of the reaction zone, a portion of the reactor bed adjacent the product removal component, and a poppet valve, wherein the surface of the poppet valve is the portion of the poppet valve that is continuously exposed to the interior region of the regenerative reverse flow reactor.

23A. The pyrolysis system of any one of paragraphs 20A to 22A, wherein the catalytic material comprises one or more of the elements from Group IVB-VIIIB and Group IA-IVA and oxides, sulfides, nitrides, carbides intermetallic and/or reduced metal species.

24A. The pyrolysis system of any one of paragraphs 20A to 23A, wherein the catalytic material is selected to provide a surface net coke deposition rate is less than 0.1 $g/m^2/hr$.

[00104] While the present invention has been described and illustrated with respect to certain embodiments, it is to be understood that the invention is not limited to the particulars disclosed and extends to all equivalents within the scope of the claims.

CLAIMS

1. A method of converting hydrocarbons into C_{2+} unsaturates comprising:

providing at least one regenerative reverse flow reactor, the regenerative reverse flow reactor having a reactor zone and at least one structural member upstream of the reaction zone; at least a portion of the inner surface of such member comprising a catalytic material that promotes the reaction of coke and/or coke precursors with hydrogen (H_2) and/or an oxidant to form vapor products;

exposing a hydrocarbon stream that contains coke and/or coke precursors to the catalytic material in the presence of hydrogen and/or an oxidant and reacting at least a portion of the coke and/or coke precursors to form vapor products; and

converting at least a portion of the hydrocarbon stream containing the hydrocarbons and the vapor products in the reaction zone to produce a reactor product having C_{2+} unsaturates.

2. The method of claim 1, further comprising exposing at least a portion of the reactor product that contains coke and/or coke precursors to at least one structural member downstream of the reaction zone, wherein at least a portion of the surface of such structural member comprises a downstream catalytic material thereon that promotes the reaction of the coke and/or coke precursors with hydrogen and/or an oxidant to form vapor products.

3. A method of converting hydrocarbons into C_{2+} unsaturates comprising:

converting a hydrocarbon stream in a reaction zone of a regenerative reverse flow reactor to produce a reactor product comprising C_{2+} unsaturates and hydrogen (H_2);

exposing at least a portion of the reactor product to at least a portion of a surface of at least one structural member having the catalytic material thereon that promotes the reaction of coke and/or coke precursors with hydrogen (H_2) and/or an oxidant at temperatures greater than 150°C; and

reacting in the presence of the catalytic material at least a portion of the coke and/or coke precursors with the hydrogen (H_2) and/or oxidant to convert the coke and/or coke precursors to vapor products.

4. The method of claim 3, wherein the at least one structural member further comprises a separator vessel upstream of the regenerative reverse flow reactor.

5. The method of any one of claims 3 or 4, further comprising exposing at least a portion of the reactor product that contains coke and/or coke precursors to at least one structural member downstream of the reaction zone, wherein at least a portion of the surface of the

structural member comprises a downstream catalytic material that promotes the reaction of the coke and/or coke precursors with hydrogen and/or an oxidant to form vapor products.

6. The method of any one of claims 3 to 5, wherein hydrogen (H_2) is added in a ratio of hydrogen to carbon (H_2/C) in the range of 0.1 to 5.0 in the hydrocarbon stream.

7. The method of claim 6, wherein the at least one structural member is one of a process tube downstream of the reaction zone, a removal component, a portion of the reactor bed adjacent the removal component, a process tube in a transfer line exchanger, and any combination thereof.

8. A method of converting hydrocarbons into C_{2+} unsaturates comprising:

converting a first hydrocarbon stream into a reactor product comprising C_{2+} unsaturates and coke in a reaction zone of a regenerative reverse flow reactor having a reactor bed and at least one structural member adjacent to an end of the reactor bed, wherein such structural member comprises one or more of a removal component and a injection component, and wherein at least a portion of the inner surface of such structural member comprises a catalytic material that promotes the reaction of coke with an oxidant;

removing a first portion of the reactor product from the reaction zone;

exposing a second portion of the of the reactor product to (i) the catalytic material and (ii) an oxidant in a stoichiometric excess amount required to react with the coke;

reacting the coke and the oxidant in the presence of the catalytic material to convert at least a portion of the coke to vapor products;

exothermically reacting the remaining oxidant with a fuel stream in the reaction zone to produce a combustion product; and

removing at least a portion of the combustion product prior to the providing a second hydrocarbon stream to the reaction zone.

9. The method of claim 8, further comprising disposing a catalytic material on at least a portion of a surface of the reactor bed adjacent the at least one structural member, wherein the catalytic material promotes the reaction of coke with the oxidant stream at temperatures less than 600°C.

10. The method of any one of claims 8 or 9, wherein the at least one structural member comprises a heat exchanger downstream of the regenerative reverse flow reactor for the combustion products.

11. The method of any one of the claims 3 to 9, wherein the converting step comprises thermally cracking the hydrocarbon stream by exposure to temperatures in the range of 1200°C to 2200°C in the reaction zone.

12. The method of any one of claims 3 to 11, wherein the at least one structural member comprises a poppet valve, wherein the surface is the portion of the poppet valve continuously exposed to an interior region of the regenerative reverse flow reactor.

13. The method of any one of claims 3 to 12, wherein the catalytic material comprises one or more of the elements from Group IVB-VIIIB and Group IA-IVA and oxides, sulfides, nitrides, carbides intermetallic and/or reduced metal species.

14. The method of any one of claims 3 to 13, wherein the catalytic material is selected to provide a surface net coke deposition rate of less than 0.1 $g/m^2/hr$.

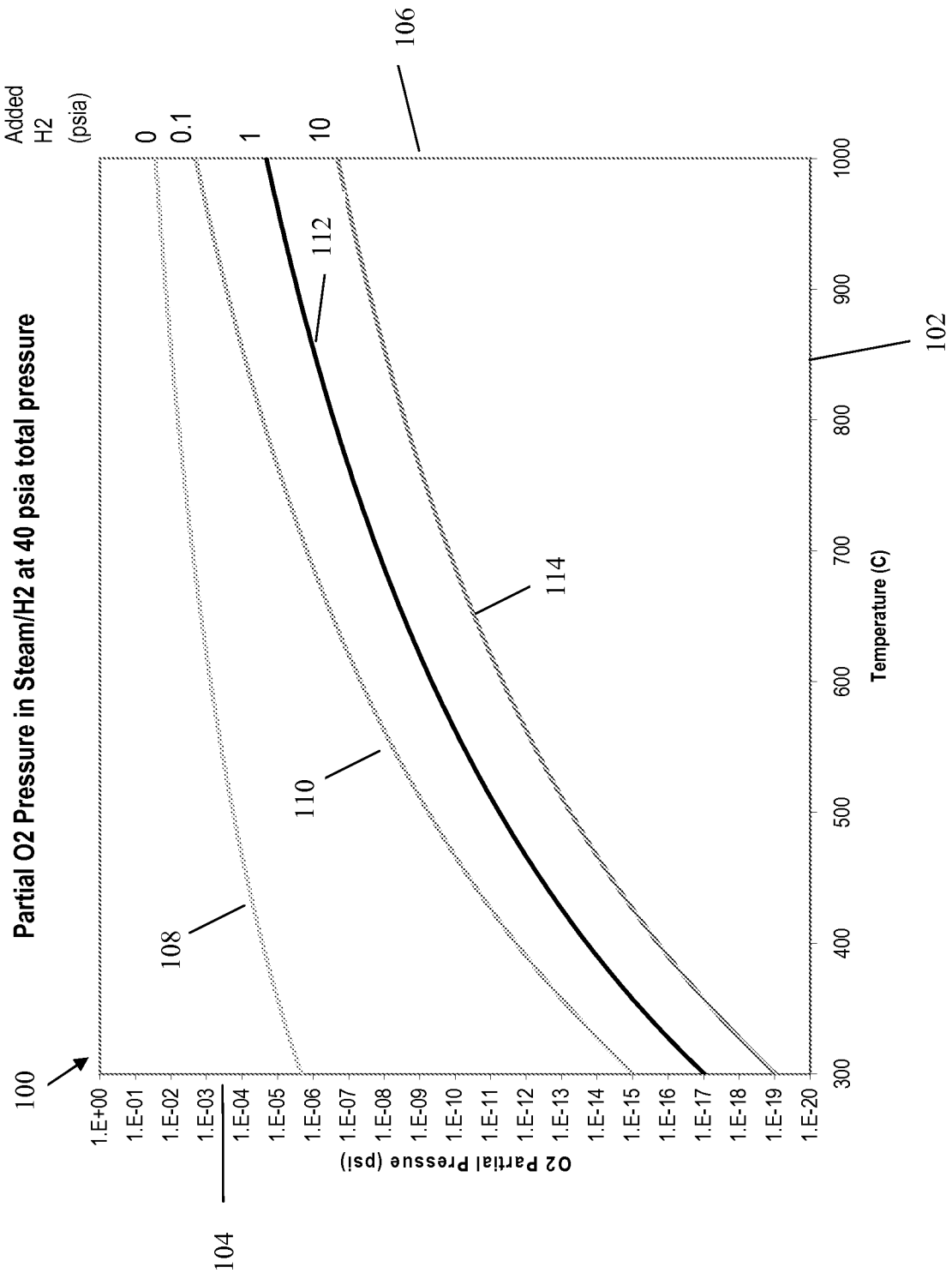
15. A pyrolysis system comprising:

a pyrolysis unit having a reaction zone, wherein the pyrolysis unit is configured to convert hydrocarbons into C_{2+} unsaturates; and

at least a portion of a surface of at least one structural member upstream of the reaction zone having a catalytic material thereon that promotes the reaction of coke and/or coke precursors with hydrogen (H_2) and/or an oxidant, wherein the pyrolysis unit is a regenerative reverse flow reactor, and wherein the at least one structural member comprises one or more of a feed injection component upstream of the regenerative reverse flow reactor, a process tube upstream of the regenerative reverse flow reactor, a poppet valve, wherein the surface is the portion of the poppet valve continuously exposed to the interior region of the regenerative reverse flow reactor, a separator vessel upstream of the regenerative reverse flow reactor, a process tube coupled between the separator vessel and the regenerative reverse flow reactor, and a heat exchanger upstream or downstream of the regenerative reverse flow reactor.

16. The pyrolysis system of claim 15, wherein the at least one structural member is one or more of a process tube downstream of the reaction zone, a removal component, a portion of the reactor bed adjacent the removal component, a process tube in a transfer line exchanger, a poppet valve, wherein the surface is the portion of the poppet valve continuously exposed to the interior region of the regenerative reverse flow reactor.

17. The pyrolysis system of any one of claims 15 or 16, wherein the catalytic material comprise one or more elements from Group IVB-VIIIB and Group IA-IVA and oxides, sulfides, nitrides, carbides intermetallic and/or reduced metal species.


Partial O2 Pressure in Steam/H2 at 40 psia total pressure
Added H2 (psia)
0
0.1
1
10
100
102
104
106
108
110
112
114
O2 Partial Pressure (psi)
1.E+00
1.E-01
1.E-02
1.E-03
1.E-04
1.E-05
1.E-06
1.E-07
1.E-08
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300
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500
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900
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Temperature (C)

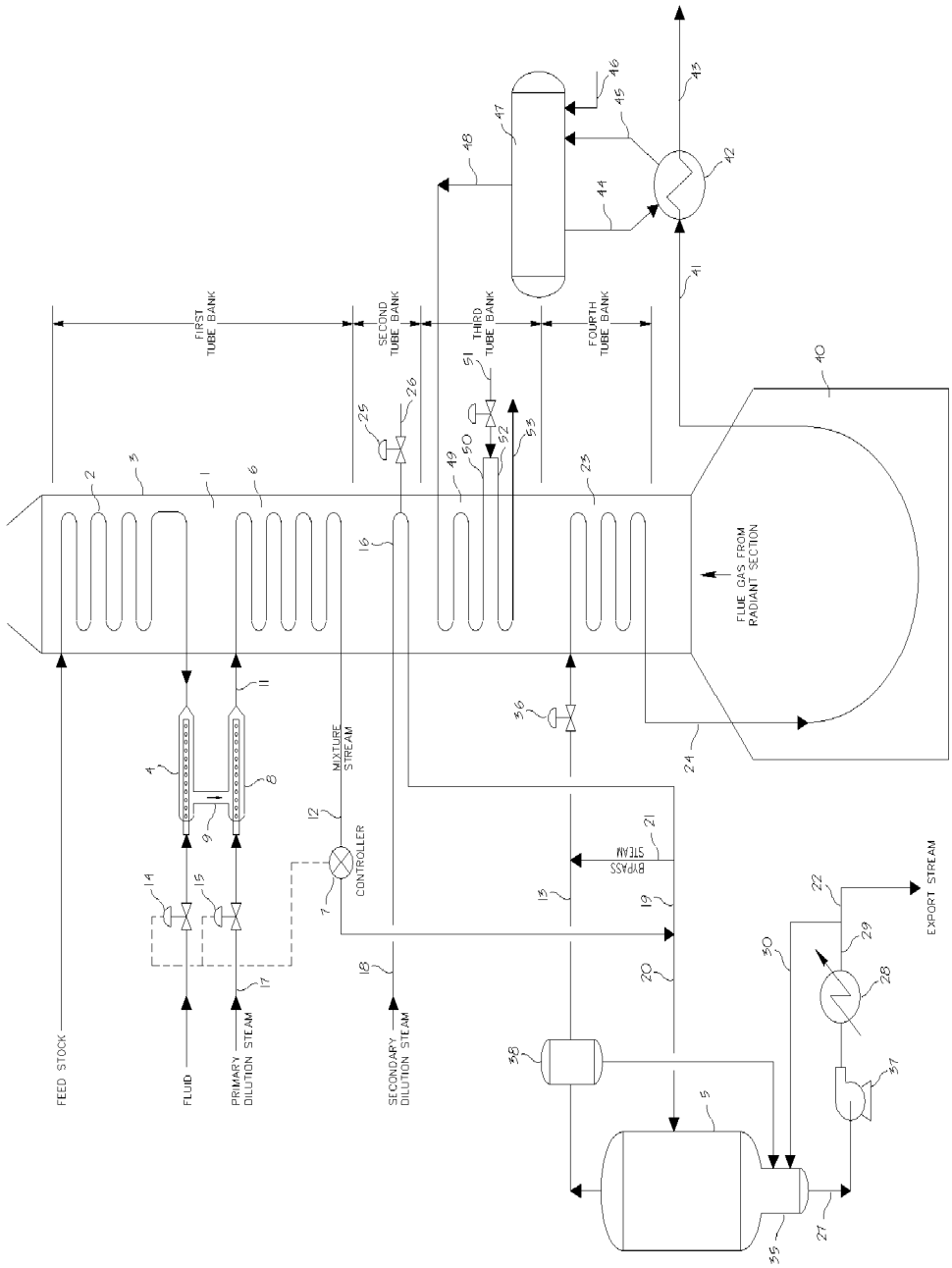

FIRST TUBE BANK
SECOND TUBE BANK
THIRD TUBE BANK
FOURTH TUBE BANK
FLUE GAS FROM RADIANT SECTION
MIXTURE STREAM
CONTROLLER
BYPASS STEAM
EXPORT STREAM
FEED STOCK
FLUID
PRIMARY DILUTION STEAM
SECONDARY DILUTION STEAM

Figure 2

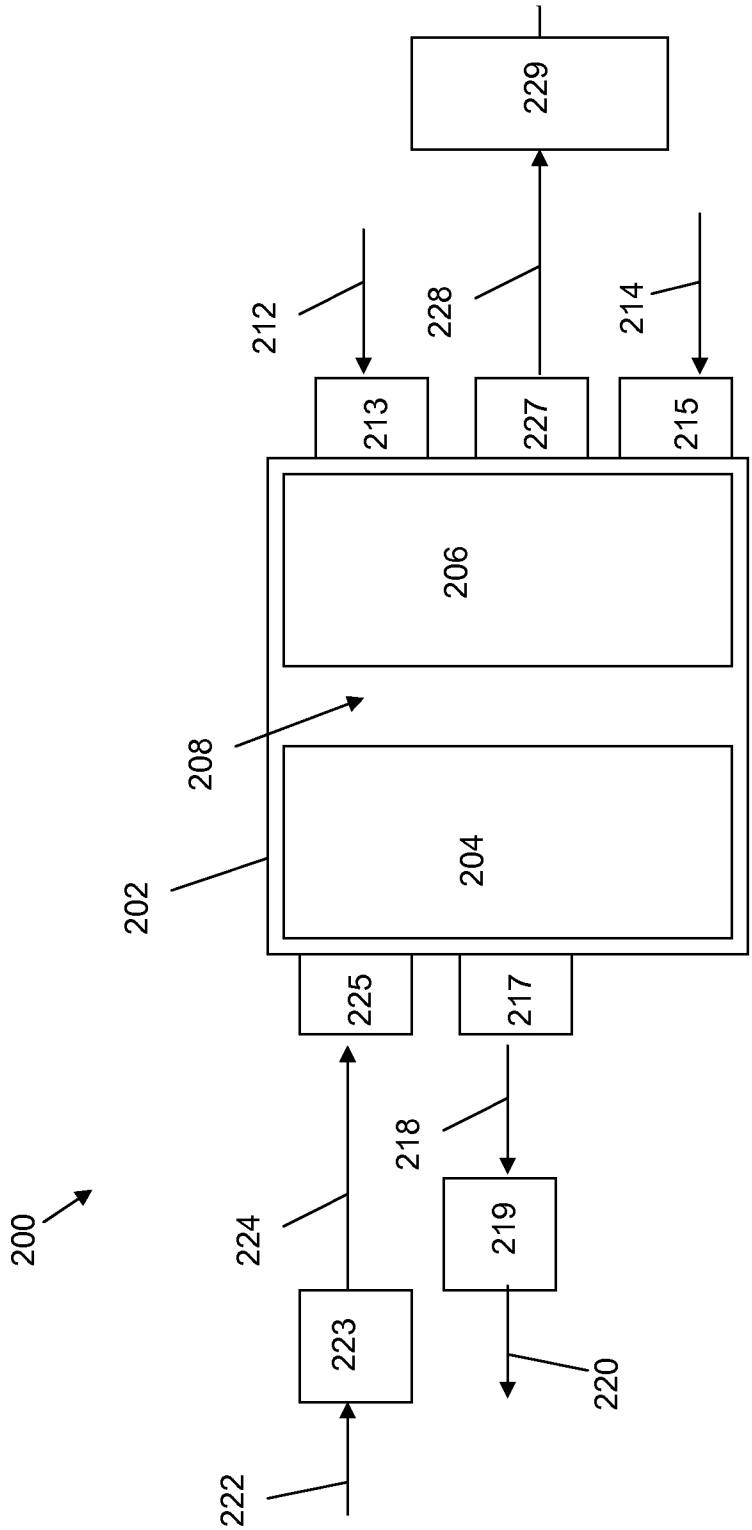

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Figure 3

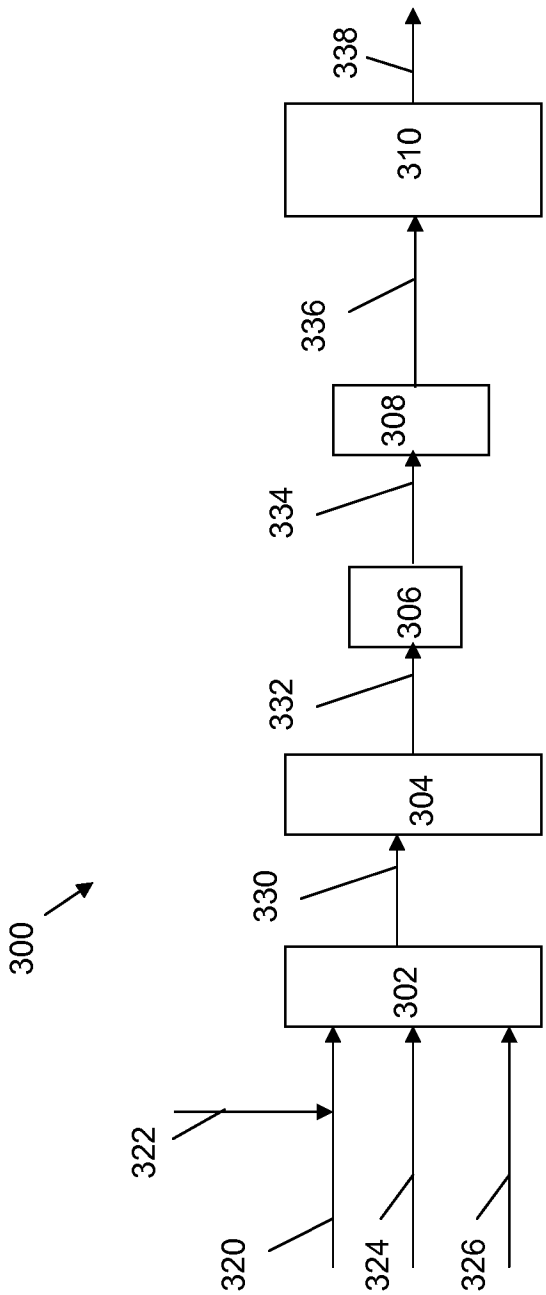


Figure 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/032735

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J8/04 C10G9/20 C10G9/16
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/144940 A1 (HERSHKOWITZ FRANK [US] ET AL) 28 June 2007 (2007-06-28)	1-17
Y	abstract paragraphs [0001] - [0004] figures 1a,1b,2 paragraphs [0050] - [0058]; example 1	3,8-11, 15
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 August 2012	22/08/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Marchand, Karin

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/032735

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 055 180 A2 (MANOIR FONDERIES ACIERIES [FR]; ELF FRANCE [FR]) 30 June 1982 (1982-06-30) abstract page 1, line 1 - page 2, line 15 page 3, line 32 - page 4, line 16 example 2; tables I-II claims 1-2,8,11-12	1-3, 8-14,17
Y	US 2003/070963 A1 (ZIMMERMANN HEINZ [DE] ET AL) 17 April 2003 (2003-04-17) paragraphs [0001], [0003], [0009] - [0013], [0018] - [0019], [0023] - [0024], [0028], [0032] claims 1-10,14-16,18-19 figure 1	1,2, 12-15,17
A	US 2006/014994 A1 (KEUSENKOTHEN PAUL F [US]) 19 January 2006 (2006-01-19) figure 1	3
A	WO 99/56062 A1 (MEGTEC SYS INC [US]) 4 November 1999 (1999-11-04) abstract page 5, lines 15-31 figure 1	12,15,16

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