



- (51) International Patent Classification:
C10G 9/36 (2006.01)
- (21) International Application Number:
PCT/US2014/031821
- (22) International Filing Date:
26 March 2014 (26.03.2014)
- (25) Filing Language:
English
- (26) Publication Language:
English
- (30) Priority Data:
13/853,802 29 March 2013 (29.03.2013) US
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- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

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(54) Title: METHODS AND APPARATUSES FOR HEATING HYDROCARBON STREAMS FOR PROCESSING

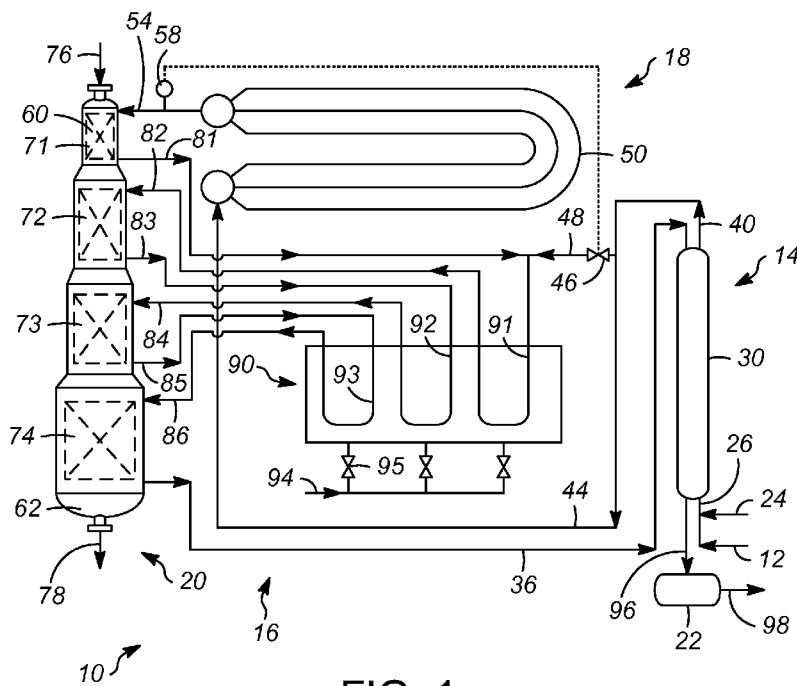


FIG. 1

(57) Abstract: Methods and apparatuses for processing hydrocarbon streams are provided. In an embodiment, a method for processing a hydrocarbon stream includes heating a feed stream in a convective bank. In the method, the feed stream is reacted in a first reaction zone to form a first effluent. The first effluent is heated in a first radiant cell that combusts fuel gas to heat the first effluent and forms a first exhaust gas. The method includes contacting the first exhaust gas with the convective bank to heat the feed stream.

WO 2014/160750 A1

Published:

— *with international search report (Art. 21(3))*

METHODS AND APPARATUSES FOR HEATING HYDROCARBON STREAMS
FOR PROCESSING

STATEMENT OF PRIORITY

[0001] This application claims priority to U.S. Application No. 13/853,802 which was filed March 29, 2013, the contents of which are hereby incorporated by reference in its entirety.

TECHNICAL FIELD

[0001] The technical field generally relates to methods and apparatuses for processing hydrocarbons, and more particularly relates to methods and apparatuses for heating hydrocarbons in convective banks for processing.

BACKGROUND

[0002] Hydrocarbon conversion processes often employ a series of reaction zones through which hydrocarbons pass. Each reaction zone may have its own unique process requirements, including a required temperature. Accordingly, each reaction zone requires a sufficient amount of heating upstream of the reaction zone to achieve the required temperature for performing the desired hydrocarbon conversion therein.

[0003] One well-known hydrocarbon conversion process is catalytic reforming. Catalytic reforming is a well-established hydrocarbon conversion process employed in the petroleum refining industry for improving the octane quality of hydrocarbon feed streams. The primary product of catalytic reforming is a gasoline blending component or a source of aromatics for petrochemicals. Reforming may be defined as the total effect produced by dehydrogenation of cyclohexanes and dehydroisomerization of alkylcyclopentanes and high carbon content C₆ to C₇ naphthenes to yield aromatics, dehydrogenation of paraffins to yield olefins, dehydrocyclization of paraffins and olefins to yield aromatics, isomerization of n-paraffins, isomerization of alkylcycloparaffins to yield cyclohexanes, isomerization of substituted aromatics, and hydrocracking of paraffins. A reforming feed stream can be a product stream from a hydrocracker, straight run, FCC, or coker, and can contain many other components such as a condensate or a thermal cracked naphtha.

[0004] Heaters or furnaces are often used in hydrocarbon conversion processes, such as reforming, to heat the process fluid before it is reacted. Generally, fired heaters or furnaces include a radiant fired heating zone to heat the fluid, with a convective section being used for another service, such as producing steam. Each section includes tubes to contain the process fluid flowing through the heater.

[0005] In view of the rising costs of fuel, conventional designs suffer disadvantages. Specifically, the production of steam by convective sections is non-optimal as steam is provided in other areas of hydrocarbon processing plants. Rather, heat from the fuel combusted in the radiant fired heating zone can be better concentrated on an increase in enthalpy in hydrocarbon processing.

[0006] Accordingly, it is desirable to provide methods and apparatuses for processing hydrocarbons utilizing convective sections to heat hydrocarbon streams. Further, it is desirable to control flow of hydrocarbon streams to convective sections and radiant fired heating zones. Also, it is desirable to provide such methods and apparatuses that operate economically. Furthermore, other desirable features and characteristics will become apparent from the subsequent detailed description and the appended claims, taken in conjunction with the accompanying drawing and the foregoing technical field and background.

BRIEF SUMMARY

[0007] Methods and apparatuses for processing hydrocarbon streams are provided. In one embodiment, a method for processing a hydrocarbon stream includes heating a feed stream in a convective bank. In the method, the feed stream is reacted in a first reaction zone to form a first effluent. The first effluent is heated in a first radiant cell that combusts fuel gas to heat the first effluent and forms a first exhaust gas. The method includes contacting the first exhaust gas with the convective bank to heat the feed stream.

[0008] In another embodiment, a method for processing hydrocarbons includes dividing the hydrocarbon stream into a first portion and a second portion according to a ratio. The first portion of the hydrocarbon stream is heated in a convective bank. The method reacts the first portion of the hydrocarbon stream in a reaction zone to form an effluent. The second portion of the hydrocarbon stream is added to the effluent. The

method includes heating the effluent in a radiant cell that forms an exhaust gas. The exhaust gas is contacted with the convective bank to heat the first portion of the hydrocarbon stream. Further, the method includes monitoring a temperature of the first portion of the hydrocarbon stream and adjusting the ratio to change an amount of the first portion flowing to the convective bank when the temperature of the first portion of the hydrocarbon stream exceeds a maximum value.

[0009] In another embodiment, an apparatus for processing a hydrocarbon stream is provided. The apparatus includes a heat exchanger configured to heat the hydrocarbon stream. A convective bank is configured to receive a first portion of the hydrocarbon stream. Further, a reaction zone is configured to receive the first portion from the convective bank and to react the first portion in a reaction zone to form an effluent. The apparatus includes a radiant cell configured to receive and heat the effluent and a second portion of the hydrocarbon stream. The radiant cell forms an exhaust gas and is configured to pass the exhaust gas to the convective bank to heat the first portion of the hydrocarbon stream. Also, the apparatus includes a temperature sensor configured to monitor a temperature of the first portion exiting the convective bank. A flow controller is configured to change an amount of the first portion flowing to the convective bank in response to the temperature of the first portion exiting the convective bank.

BRIEF DESCRIPTION OF THE DRAWING

[0010] Embodiments of methods and apparatuses for processing hydrocarbons will hereinafter be described in conjunction with the following drawing figure wherein:

[0011] FIG. 1 is a schematic diagram of an embodiment of a method and apparatus for heating hydrocarbons for processing in accordance with an embodiment;

[0012] FIG. 2 is a schematic diagram illustrating the flow of exhaust gas from the radiant zone to the convective zone of the embodiment of FIG. 1; and

[0013] FIG. 3 is a schematic diagram illustrating details of the convective zone of the embodiment of FIG. 1.

DETAILED DESCRIPTION

[0014] The following detailed description is merely exemplary in nature and is not intended to limit the methods or apparatuses for processing hydrocarbons. Furthermore, there is no intention to be bound by any theory presented in the preceding background or the following detailed description.

[0015] Methods and apparatuses for processing hydrocarbon streams, and more particularly, for heating hydrocarbon streams in convective sections upstream of reaction zones are provided herein. The methods and apparatuses reduce fuel costs for radiant fired heating zones, as increased amounts of energy produced from combustion of the fuel is transferred to the hydrocarbon streams through convective sections. As used herein, the phrase "hydrocarbon stream" includes any stream including various hydrocarbon molecules, such as straight-chain, branched, or cyclic alkanes, alkenes, alkadienes, and alkynes, and optionally other substances including gases, such as hydrogen. The hydrocarbon stream may be subject to reactions, for example, reforming reactions, but still may be referred to as a hydrocarbon stream, as long as at least some hydrocarbons are present in the stream after the reaction. Thus, the hydrocarbon stream may include streams that are subjected to one or more reactions, e.g., a hydrocarbon stream effluent, or not subjected to any reactions, e.g., a naphtha feed. As used herein, a hydrocarbon stream can also include a raw hydrocarbon feed stream, a combined feed stream, or an effluent.

[0016] The methods and apparatuses for heating hydrocarbons for processing as described herein are particularly applicable to processes utilizing at least two reaction zones, where at least a portion of the hydrocarbon stream flows serially through the reaction zones. Processes having multiple reaction zones may include a wide variety of hydrocarbon conversion processes such as reforming, hydrogenation, hydrotreating, dehydrogenation, isomerization, dehydroisomerization, dehydrocyclization, cracking, and hydrocracking processes. Catalytic reforming often utilizes multiple reaction zones, and will be referenced hereinafter in the embodiments depicted in the drawings. However, the claimed methods and apparatuses are not limited for catalytic reforming processes.

[0017] The drawings illustrate an embodiment of a method and apparatus for hydrocarbon processing as applied to a catalytic reforming process. The drawings are presented solely for purposes of illustration and are not intended to limit the scope of the

claims as set forth below. The drawings show only the equipment and lines necessary for an understanding of various embodiments herein and do not show equipment such as pumps, compressors, heat exchangers, and valves which are not necessary for an understanding of the methods and apparatuses claimed herein and which are well known to persons of ordinary skill in the art of hydrocarbon processing.

[0018] Referring to FIG. 1, an apparatus 10 for processing a hydrocarbon feed stream 12 is schematically depicted. The exemplary apparatus 10 is a reforming unit including a heat exchange section 14, a radiant fired heating section 16, a convective heating section 18, a reaction section 20, and a product recovery section 22.

[0019] As shown, the hydrocarbon feed stream 12 flows to the heat exchange section 14 upstream of sections 16, 18 and 20. An exemplary hydrocarbon feed stream 12 for catalytic reforming is a petroleum fraction known as naphtha, having an initial boiling point of 82°C (180°F) and an end boiling point of 203°C (400°F). The catalytic reforming process is particularly applicable to the treatment of straight run naphthas comprised of relatively large concentrations of naphthenic and substantially straight chain paraffinic hydrocarbons, which are subject to aromatization through dehydrogenation and/or cyclicization reactions. Exemplary charge stocks are naphthas consisting principally of naphthenes and paraffins that can boil within the gasoline range, although, in many cases, aromatics also can be present. This class of naphthas includes straight-run gasolines, natural gasolines, synthetic gasolines, and the like. Other embodiments may charge thermally or catalytically cracked gasolines or partially reformed naphthas. Mixtures of straight-run and cracked gasoline-range naphthas can also be used to advantage. The gasoline-range naphtha charge stock may be a full-boiling gasoline having an initial boiling point of 40°C to 82°C (104°F to 180°F) and an end boiling point within the range of 160°C to 220°C (320°F to 428°F), or may be a selected fraction thereof which generally can be a higher-boiling fraction commonly referred to as a heavy naphtha, for example, a naphtha boiling in the range of 100°C to 200°C (212°F to 392°F). In some cases, it is also advantageous to charge pure hydrocarbons or mixtures of hydrocarbons that have been recovered from extraction units, for example, raffinates from aromatics extraction or straight-chain paraffins, which are to be converted to aromatics. In some other cases, the feed stream 12 may also contain light hydrocarbons that have 1-5 carbon atoms, but since

these light hydrocarbons cannot be readily reformed into aromatic hydrocarbons, these light hydrocarbons entering with the feed stream 12 are generally minimized.

[0020] As is typical for catalytic reforming processes, the feed stream 12 is admixed with a recycled stream 24 comprising hydrogen to form what is commonly referred to as a combined feed stream 26 before being delivered to a combined feed heat exchanger 30 in the heat exchange section 14. Generally, the recycled stream 24 supplies hydrogen in an amount of 1 to 20 moles of hydrogen per mole of hydrocarbon feed stream 12. For example, hydrogen may be supplied to provide an amount of less than 3.5 moles of hydrogen per mole of hydrocarbon feed stream 12. If hydrogen is supplied, it may be supplied upstream of the combined feed heat exchanger 30, downstream of the combined feed heat exchanger 30, or both upstream and downstream of the combined feed heat exchanger 30. Alternatively, no hydrogen may be supplied. Even if hydrogen is not provided to the hydrocarbon feed stream 12, naphthene reforming reactions that occur within the reaction section 20 can yield hydrogen as a by-product. This by-product, or in-situ-produced, hydrogen can become available as hydrogen downstream reaction zones within the reaction section 20. In situ hydrogen in the reaction section 20 may total from 0.5 to 2 moles of hydrogen per mole of hydrocarbon feed stream 12.

[0021] In the combined feed heat exchanger 30, the combined feed stream 26 can be heated by exchanging heat with the product effluent 36 of the reaction section 20. However, the heating of the combined feed stream 26 that occurs in the combined feed heat exchanger 30 is generally insufficient to heat the combined feed stream 26 to the desired inlet temperature of the reaction section 20. In a typical catalytic reforming process, the combined feed stream 26, or the hydrocarbon feed stream 12 if no hydrogen is provided with the hydrocarbon feed stream 12, enters the combined feed heat exchanger 30 at a temperature of generally 38°C to 177°C (100°F to 350°F), and more usually 93°C to 121°C (200°F to 250°F). Generally, the combined feed heat exchanger 30 heats the combined feed stream 26 by transferring heat from the product effluent 36 of the last reforming reaction zone in the reaction section 20 to the combined feed stream 26. An exemplary combined feed heat exchanger 30 is an indirect, rather than a direct, heat exchanger, in order to prevent valuable reformate product in the product effluent 36 from intermixing with the combined feed stream 26, and thereby being recycled to the reaction section 20, where the reformate quality could be degraded.

[0022] In an exemplary embodiment, the flow pattern of the combined feed stream 26 and the product effluent 36 within the combined feed heat exchanger 30 is countercurrent, through it could be completely cocurrent, reversed, mixed, or cross flow. In a countercurrent flow pattern, the combined feed stream 26, while at its coldest temperature, contacts one end (i.e., the cold end) of the heat exchange surface of the combined feed heat exchanger 30 while the product effluent 36 contacts the cold end of the heat exchange surface at its coldest temperature as well. Thus, the product effluent 36, while at its coldest temperature within the heat exchanger, exchanges heat with the combined feed stream that is also at its coldest temperature within the heat exchanger. At another end (i.e., the hot end) of the combined feed heat exchanger surface, the product effluent 36 and the combined feed stream, both at their hottest temperatures within the heat exchanger, contact the hot end of the heat exchange surface and thereby exchange heat. Between the cold and hot ends of the heat exchange surface, the product effluent 36 and the combined feed stream flow in generally opposite directions, so that, in general, at any point along the heat transfer surface, the hotter the temperature of the product effluent 36, the hotter is the temperature of the combined feed stream with which the product effluent 36 exchanges heat. The exemplary combined feed heat exchanger 30 operates with a hot end approach that is generally less than 56°C (100°F), such as less than 33°C (60°F), for example, less than 28°C (50°F).

[0023] Although the combined feed heat exchanger 30 may utilize shell-and-tube type heat exchangers, it may alternatively use plate type heat exchangers. Plate type exchangers are well known and commercially available in several different and distinct forms, such as spiral, plate and frame, brazed-plate fin, and plate fin-and-tube types.

[0024] In one embodiment, the combined feed stream 26 leaves the combined feed heat exchanger 30 as a heated feed stream 40 at a temperature of 399°C to 516°C (750°F to 960°F). Because the reforming reactions that occur first in the reaction zone 60 take place at an elevated temperature and are generally endothermic, the feed stream 40 often requires additional heating after exiting the combined feed heat exchanger 30 and prior to entering the reaction section 20.

[0025] In prior art apparatuses, this additional heating is provided in a radiant cell such as a charge heater, for example, a gas-fired, oil-fired, or mixed gas-and-oil-fired heater,

that heats the feed stream 40 by radiant or radiant and convective heat transfer. It is contemplated herein that, as desired, a portion of the feed stream 40 may selectively bypass any radiant heating zone and instead be heated in the convective heating section 18 without passing through a radiant heater. Therefore, a first portion 44 of the feed stream 40 is selectively delivered to the convective heating section 18. Specifically, a valve 46 is utilized to control the division of feed stream 40 into the first portion 44 and a second portion 48. For example, the valve 46 may be closed to direct the entirety of feed stream 40 to the convective heating section 18 as the first portion 44. When the valve 46 is opened, a selected amount of the feed stream 40 flows to the radiant heating section 16 as the second portion, while an amount continues to flow to the convective heating section 18 as the first portion 44.

[0026] In the convective heating section 18, the first portion 44 flows through a convective heat bank 50 as described further in relation to FIG. 2 below. The first portion 44 is typically heated to a temperature of 482°C to 560°C (900°F to 1,040°F), such as 493°C to 549°C (920°F to 1,020°F). As shown, the convectively heated stream 54 exits the convective heating section 18 and flows to the reaction section 20. A temperature indicator/controller 58 is in communication with the convectively heated stream 54 upstream of the reaction section 20. Further, the temperature indicator/controller 58 is in electronic communication with the valve 46. The temperature indicator/controller 58 monitors the temperature of the convectively heated stream 54. When the temperature exceeds a predetermined maximum temperature, such as 549°C (1020°F), the temperature indicator/controller 58 directs the valve 46 to close to increase the percentage of the feed stream 40 delivered to the convective heating section 18 as the first portion 44, thereby increasing the flow rate of the first portion 44 through the convective heat bank 50 and reducing the temperature of the convectively heated stream 54 exiting the convective heat bank 50. When the temperature indicator/controller 58 senses that the temperature of the convectively heated stream 54 exiting the convective heat bank 50 has decreased to below a predetermined minimum temperature, such as 546°C (1015°F), the temperature indicator/controller 58 directs the valve 46 to open to decrease the percentage of the feed stream 40 delivered to the convective heating section 18 as the first portion 44, thereby decreasing the flow rate of the first portion 44 through the convective heat bank 50 and

increasing the temperature of the convectively heated stream 54 exiting the convective heat bank 50.

[0027] As shown, the convectively heated stream 54 enters the exemplary reaction section 20 which includes four reaction zones 60 through which hydrocarbons flow serially. Reaction sections having multiple reaction zones 60 generally take one of two forms: a stacked form as shown in FIG. 1 or a side-by-side form. In the side-by-side form, multiple and separate reaction vessels, each that can include a reaction zone, may be placed beside each other. In the stacked form, one common reaction vessel 62 contains multiple and separate reaction zones 60 that are placed on top of each other. In either arrangement, there can be intermediate heating or cooling between the reaction zones 60, depending on whether the reactions are endothermic or exothermic.

[0028] The exemplary catalytic reforming process utilizes a reaction section 20 with a first reaction zone 71, a second reaction zone 72, a third reaction zone 73, and a fourth reaction zone 74. There may be any number of reaction zones 60, but usually the number of reaction zones 60 is three, four or five. Hydrocarbons undergo conversion reactions in each reaction zone 60, in the presence of catalyst particles 76. The exemplary reforming process employs catalyst particles 76 in the reaction zones 62 in a series flow arrangement, and spent catalyst particles 78 may exit the reaction section 20 as shown.

[0029] In overview, the first reaction zone 71 receives the convectively heated stream 54 as a first reactor feed and produces a first effluent 81. Endothermic reforming reactions that occur in the first reaction zone 71 generally cause the outlet temperature of the first reaction zone 71 to fall not only to less than the temperature of the convectively heated stream 54, but also to less than the desired inlet temperature of the second reaction zone 72. Therefore, the first effluent 81 is heated in the radiant fired heating section 16 to the desired inlet temperature of the second reaction zone 72 as discussed below and is returned to the reaction section 20 as second reactor feed 82. The second reaction zone 72 reacts the second reactor feed 82 to form a second effluent 83. Again, due to endothermic reactions, the second effluent 83 requires heating to reach the desired inlet temperature of the third reaction zone 73. The second effluent 83 flows to and is heated by the radiant fired heating section 16 as discussed below and is returned to the reaction section 20 as a third reactor feed 84. The third reaction zone 73 reacts the third reactor feed 84 to form a

third reactor effluent 85. As above, endothermic reactions may cause the temperature of the third reactor effluent 85 to fall below the desired inlet temperature of the fourth reaction zone 74. The third reactor effluent 85 flows to and is heated by the radiant fired heating section 16 as discussed below and is returned to the reaction section 20 as a fourth reactor feed 86. The fourth reaction zone 74 reacts the fourth reactor feed 86 to form the product effluent 36.

[0030] Exemplary reaction zones 60 can be operated at reforming conditions, which include a range of pressures generally from atmospheric pressure of 0 to 6,895 kpag (0 psig to 1,000 psig), with particularly good results obtained at the relatively low pressure range of 276 to 1,379 kpag (40 to 200 psig). The overall liquid hourly space velocity (LHSV) based on the total catalyst volume in all of the reaction zones is generally 0.1 hr⁻¹ to 10 hr⁻¹, such as 1 hr⁻¹ to 5 hr⁻¹, for example, 1.5 hr⁻¹ to 2.0 hr⁻¹.

[0031] Generally naphthene reforming reactions that are endothermic occur in the first reaction zone 71, and thus the outlet temperature of the first reaction zone 71 can be less than the inlet temperature of the first reaction zone 71 and is generally 316°C to 454°C (600°F to 850°F). The first reaction zone 71 may contain generally 5% to 50%, and more usually 10% to 30%, of the total catalyst volume in all of the reaction zones 60. Consequently, the liquid hourly space velocity (LHSV) in the first reaction zone 71, based on the catalyst volume in the first reaction zone 71, can be generally 0.2-200 hr⁻¹, such as 2 hr⁻¹ to 100 hr⁻¹, for example 5 hr⁻¹ to 20 hr⁻¹. Generally, the catalyst particles are withdrawn from the first reaction zone 71 and passed to the second reaction zone 72. The particles generally have a coke content of less than 2 wt% based on the weight of catalyst.

[0032] An exemplary catalytic conversion process includes catalyst particles 76 that are movable through the reaction zones 60. The catalyst particles 76 may be movable through the reaction zones 60 by any number of motive devices, including conveyors or transport fluid, but most commonly the catalyst particles 76 are movable through the reaction zones 60 by gravity. Catalyst particles 76 can be withdrawn from a bottom portion of an upper reaction zone and introduced into a top portion of a lower reaction zone. The spent catalyst particles 78 withdrawn from the final reaction zone can subsequently be recovered from the process, regenerated in a regeneration zone (not shown) of the process, or transferred to another reaction zone 60. Likewise, the catalyst

particles 76 added to a reaction zone can be catalyst that is being newly added to the process, catalyst that has been regenerated in a regeneration zone within the process, or catalyst that is transferred from another reaction zone 60.

[0033] Exemplary reforming reactions are normally effected in the presence of catalyst particles 76 comprised of one or more Group VIII (IUPAC 8-10) noble metals (e.g., platinum, iridium, rhodium, and palladium) and a halogen combined with a porous carrier, such as a refractory inorganic oxide. Although the catalyst may contain 0.05 to 2.0 wt% of Group VIII metal, a less expensive catalyst, such as a catalyst containing 0.05 to 0.5 wt% of Group VIII metal may be used. An exemplary noble metal is platinum. In addition, the catalyst may contain indium and/or a lanthanide series metal such as cerium. The catalyst particles 76 may also contain 0.05 to 0.5 wt% of one or more Group IVA (IUPAC 14) metals (e.g., tin, germanium, and lead). An exemplary halogen is chlorine and an exemplary carrier is alumina. Exemplary alumina materials are gamma, eta, and theta alumina, with gamma and eta alumina generally being used in selected embodiments.

[0034] A reforming process can employ a fixed catalyst bed, or a moving bed reaction vessel and a moving bed regeneration vessel. In the latter, generally regenerated catalyst particles 76 are fed to the reactor vessel 62, typically including several reaction zones 60, and the catalyst particles 76 flow through the reaction vessel 62 by gravity. During the course of a reforming reaction with a moving catalyst bed, catalyst particles become deactivated as a result of mechanisms such as the deposition of coke on the particles; that is, after a period of time in use, the ability of catalyst particles to promote reforming reactions decreases to the point that the catalyst is no longer useful. The catalyst can be reconditioned, or regenerated, before it is reused in a reforming process.

[0035] Specifically, catalyst may be withdrawn from the bottom of the reaction vessel 62 and transported to a regeneration vessel. In the regeneration vessel, a multi-step regeneration process is typically used to regenerate the catalyst to restore its full ability to promote reforming reactions. Catalyst can flow by gravity through the various regeneration steps and then be withdrawn from the regeneration vessel and transported to the reaction vessel 62. Generally, arrangements are provided for adding fresh catalyst as make-up to and for withdrawing spent catalyst particles 78 from the process. Movement of catalyst through the reaction and regeneration vessels is often referred to as continuous

though, in practice, it is semi-continuous. In semi-continuous movement, relatively small amounts of catalyst are repeatedly transferred at closely spaced intervals. For example, one batch every twenty minutes may be withdrawn from the bottom of the reaction vessel 62 and withdrawal may take five minutes, that is, catalyst can flow for five minutes. If the catalyst inventory in a vessel is relatively large in comparison with this batch size, the catalyst bed in the vessel may be considered to be continuously moving. A moving bed system can have the advantage of maintaining production while the catalyst is removed or replaced. Typically, the rate of catalyst movement through the catalyst beds may range from as little as 45.5 kg (100 pounds) per hour to 2,722 kg (6,000 pounds) per hour, or more.

[0036] As shown in FIG. 1, downstream of the first reaction zone 71, hydrocarbons flow between the reaction zones 60 and radiant cells 90 in the radiant fired heating section 16. For example, the first effluent 81 exits the reaction section 20 and is mixed with the second portion 48 of the heated feed stream 40, if the amount of the second portion 48 passing through valve 46 is greater than zero. The first effluent 81 (and second portion 48) then flows into a first radiant cell 91 where it is heated and forms the second reactor feed 82. The second effluent 83 exits the reaction section 20 and flows into a second radiant cell 92 where it is heated and forms the third reactor feed 84. Likewise, the third effluent 85 exits the reaction section 20 and flows into a third radiant cell 93 where it is heated and forms the fourth reactor feed 86.

[0037] Effluent flow between reaction zones and radiant cells may typically occur with a flat temperature profile on the reaction zone inlets, i.e., heated effluent is the same temperature at all reaction zone inlets. Alternately, effluent flow may be managed with a graduated temperature profile. In either case, each radiant cell 90 (typically referred to as an interheater when it is located between two reaction zones 60) is heated by combustion of a fuel gas 94, selectively delivered to the radiant cell 90 by a valve 95 to heat the respective effluent to a same temperature.

[0038] As in the first reaction zone 71, endothermic reactions can cause another decline in temperature across the second reaction zone 72. Generally, however, the temperature decline across the second reaction zone 72 is less than the temperature decline across the first reaction zone 71, because the reactions that occur in the second reaction

zone 72 are generally less endothermic than the reactions that occur in the first reaction zone 71. Despite the somewhat lower temperature decline across the second reaction zone 72, the second effluent 83 is nevertheless still at a temperature that is less than the desired inlet temperature of the third reaction zone 73. Thus, the second effluent is heated in the second radiant cell 92 to form the third reactor feed 84.

[0039] The second reaction zone 72 generally includes 10% to 60%, and more usually 15% to 40%, of the total catalyst volume in all of the reaction zones 60. Consequently, the liquid hourly space velocity (LHSV) in the second reaction zone 72, based on the catalyst volume in the second reaction zone, is generally 0.13 hr⁻¹ to 134 hr⁻¹, such as 1.3 hr⁻¹ to 67 hr⁻¹, for example 3.3 hr⁻¹ to 13.4 hr⁻¹.

[0040] In the third reaction zone 73, endothermic reactions can cause another decline in temperature, though it is typically less than the temperature decline across the first reaction zone 71 as the reactions in the third reaction zone 73 are generally less endothermic. The third reaction zone 73 contains generally 25% to 75%, and more usually 30% to 50%, of the total catalyst volume in all of the reaction zones 60. In order to raise the temperature of the third effluent 85, it is heated in the third radiant cell 93.

[0041] In an exemplary embodiment, each effluent 81, 83, and 85 enters and exits the top portion of each radiant cell 91, 92, and 93 through U-shaped tubes. Alternatively, each effluent 81, 83, 85 may enter and exit a lower portion of each radiant cell through inverted U-shaped tubes, or enter the top portion where the temperature is lowest in a radiant cell and exit at the bottom where the temperature is hottest in the radiant cell, or conversely, enter at the bottom and exit at the top. Of course, while U-shaped tubes are illustrated, there are many radiant cell coil configurations or layouts that can be utilized for radiant heating of the effluent.

[0042] After heating in the third interheater 93, the fourth reactor feed 86 is delivered to the fourth reaction zone 74. The fourth reaction zone 74 contains generally 30% to 80%, and more usually 40% to 50%, of the total catalyst volume in all of the reaction zones 60. The inlet temperatures of the third, fourth, and subsequent reaction zones are generally 482°C to 560°C (900 to 1,040°F), such as 493°C to 549°C (920°F to 1,020°F).

[0043] Because the reforming reactions that occur in the second and subsequent (i.e., third and fourth) reaction zones 60 are generally less endothermic than those that occur in

the first reaction zone 71, the temperature drop that occurs in the later reaction zones 60 is generally less than that that occurs in the first reaction zone 71. Thus, the outlet temperature of the last reaction zone 74 may be 11°C (20°F) or less below the inlet temperature of the last reaction zone 74, and indeed may conceivably be higher than the inlet temperature of the last reaction zone 74. Moreover, any inlet temperature profiles can be utilized with the above-described reaction zones 60. The inlet temperature profiles can be flat or skewed, such as ascending, descending, hill-shaped, or valley-shaped. Desirably, the inlet temperature profile of the reaction zones 60 is flat.

[0044] As shown, the product effluent 36 is cooled in the combined feed heat exchanger 30 by transferring heat to the combined feed stream 26. After leaving the combined feed heat exchanger 30, the cooled product effluent 96 passes to the product recovery section 22. Suitable product recovery sections 22 are well-known. The exemplary product recovery section 22 may include a gas-liquid separator for separating hydrogen and C1-C3 hydrocarbon gases from the product effluent 36, and fractionation columns for separating at least a portion of the C4-C5 light hydrocarbons from the remainder of the reformat. In addition, the reformat may be separated by distillation into a light reformat fraction and a heavy reformat fraction. As a result of product recovery processes, a product stream 98 is formed, or multiple product streams 98 are formed, containing desired species.

[0045] Referring now to FIG. 2, heat transfer between the radiant fired heating section 16 and the convective heating section 18 is explained. As shown, each radiant cell 90 includes a radiant tube 102 having an inlet 104 and an outlet 106, and may be somewhat U-shaped and orientated upwardly. Although only one radiant tube is illustrated for each radiant cell 90, it should be understood that generally each radiant cell 90 can include an inlet manifold, a series of tubes, and an outlet manifold. A series of radiant tubes 102 may be configured in a parallel configuration and can be stacked front-to-back. The radiant cells 90 can be separated by firewalls 112 and include, respectively, at least one burner 122.

[0046] As effluent streams pass through each respective radiant cell 90, fuel gas 94 is combusted in the burner 122 and forms a flue gas, indicated by arrows 130. The flue gas 130 rising from the radiant cells 90 can enter the convective heat bank 50 in the

convective heating section 18 through an inlet or inlets 132 and exit through a stack 134. The convective heat bank 50 generally includes several convective tubes 138 in a parallel configuration. Each convective tube 138 has an inlet 142 and an outlet 144 and can be somewhat U-shaped and orientated sideways. For a plurality of convective tubes 138, tubes 138 can be stacked front-to-back in rows. Although convective tubes 138 can be oriented beside one another, it should be understood that other orientations are possible, such as orienting the U-shaped tubes flat and stacking several tubes 138 vertically in rows.

[0047] The portion 44 of the feed stream entering the convective heating section 18 enters the inlet 142 of the convective tube 138 and is convectively heated by thermal transfer from the flue gases 130 through the convective tubes 138. While the inlet 142 is indicated as being above the outlet 144 such that the portion 44 enters the top portion where the temperature is lowest in the convective heating section 18 and exits at the bottom where the temperature is hottest in the convective heating section 18 through the sideways-oriented U-shaped tubes 138, other configurations are contemplated. For example, the portion 44 may enter and exit the top or lower portion of the convective section 138, or enter at the bottom and exit at the top.

[0048] FIG. 3 illustrates an exemplary convective heat bank 50 in which the convective tubes 138 includes shock tubes 152 and finned tubes 154. Specifically, the convective heat bank 50 includes three rows 156 of shock tubes 152 below three rows 158 of finned tubes 154. Such an arrangement may provide for more efficient heat transfer from the rising flue gases 130 to the portion 44 of the feed stream 40 flowing through the tubes 138. Specifically, the finned tubes 154 positioned in the upper cooler portion of the convective heat bank 50 are adapted for more efficient heat transfer while the shock tubes 152 positioned in the lower hotter portion of the convective heat bank 50 are better able to endure hotter temperatures.

[0049] As described herein, an apparatus and method for heating a hydrocarbon stream for processing have been provided. In exemplary embodiments, an apparatus and method have been described for catalytic reforming processes, though any suitable apparatuses and methods for processing hydrocarbons may utilize the heating process disclosed herein. Although the embodiments discussed above can be designed for a new

hydrocarbon processing apparatus, it should be understood that the disclosed features can be implemented during the revamp of an existing apparatus

[0050] While at least one exemplary embodiment has been presented in the foregoing detailed description, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the claimed subject matter in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment or embodiments. It being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without departing from the scope set forth in the appended claims.

SPECIFIC EMBODIMENTS

[0051] While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

[0052] A first embodiment of the invention is a method for processing a hydrocarbon stream, the method comprising the steps of heating a feed stream in a convective bank; reacting the feed stream in a first reaction zone to form a first effluent; heating the first effluent in a first radiant cell, wherein the first radiant cell combusts fuel gas to heat the first effluent and forms a first exhaust gas; and contacting the first exhaust gas with the convective bank to heat the feed stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising dividing the feed stream into a first portion and a second portion, wherein heating a feed stream in a convective bank comprises heating the first portion of the feed stream in a convective bank, wherein reacting the feed stream in a first reaction zone to form a first effluent comprises reacting the first portion of the feed stream in a first reaction zone to form a first effluent, and wherein the method further comprises mixing the second portion of the feed stream with the first effluent before heating the first effluent in a first radiant cell. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein

dividing the feed stream into a first portion and a second portion comprises monitoring a temperature of the feed stream exiting the convective bank; and selectively increasing an amount of the first portion of the feed stream flowing to the convective bank in response to the temperature of the feed stream exiting the convective bank. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the first reaction zone has a required inlet temperature and wherein dividing the feed stream into a first portion and a second portion comprises monitoring a temperature of the feed stream exiting the convective bank to determine whether the temperature exceeds the required inlet temperature; and selectively increasing an amount of the first portion of the feed stream flowing to the convective bank if the temperature exceeds the required inlet temperature. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the convective bank comprises shock tube rows and/or finned tube rows, and wherein heating the feed stream in a convective bank comprises heating the feed stream in the shock tube rows and/or in the finned tube rows. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising adding a recycled gas stream comprising hydrogen to the feed stream before heating the feed stream in the convective bank. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising reacting the first effluent in a second reaction zone to form a second effluent; heating the second effluent in a second radiant cell, wherein the second radiant cell combusts fuel gas to heat the second effluent and forms a second exhaust gas; contacting the second exhaust gas with the convective bank to heat the feed stream; reacting the second effluent in a third reaction zone to form a third effluent; heating the third effluent in a third radiant cell, wherein the third radiant cell combusts fuel gas to heat the third effluent and forms a third exhaust gas; contacting the third exhaust gas with the convective bank to heat the feed stream; and reacting the third effluent in a fourth reaction zone to form a product effluent. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising dividing the feed stream into a first portion and a second portion, wherein heating the feed stream in a convective bank comprises heating the first portion of the feed stream in a convective

bank, wherein reacting the feed stream in a first reaction zone to form a first effluent comprises reacting the first portion of the feed stream in a first reaction zone to form a first effluent, and wherein the method further comprises mixing the second portion of the feed stream with the first effluent before heating the first effluent in a first radiant cell. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising passing the product effluent through a heat exchanger; and heating the feed stream in the heat exchanger before heating the feed stream in the convective bank. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising condensing the product effluent to form a product stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising dividing the feed stream into a first portion and a second portion, wherein heating a feed stream in a convective bank comprises heating the first portion of the feed stream in a convective bank, wherein reacting the feed stream in a first reaction zone to form a first effluent comprises reacting the first portion of the feed stream in a first reaction zone to form a first effluent, and wherein the method further comprises mixing the second portion of the feed stream with the first effluent before heating the first effluent in a first radiant cell. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein dividing the feed stream into a first portion and a second portion comprises monitoring a temperature of the feed stream exiting the convective bank; and selectively increasing an amount of the first portion of the feed stream flowing to the convective bank in response to the temperature of the feed stream exiting the convective bank. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the first reaction zone has a required inlet temperature and wherein dividing the feed stream into a first portion and a second portion comprises monitoring a temperature of the feed stream exiting the convective bank to determine whether the temperature exceeds the required inlet temperature; selectively increasing an amount of the first portion of the feed stream flowing to the convective bank if the temperature exceeds the required inlet temperature.

[0053] A second embodiment of the invention is a method for processing a hydrocarbon stream, the method comprising the steps of dividing the hydrocarbon stream into a first portion and a second portion according to a ratio; heating the first portion of the hydrocarbon stream in a convective bank; reacting the first portion of the hydrocarbon stream in a reaction zone to form an effluent; adding the second portion of the hydrocarbon stream to the effluent; heating the effluent in a radiant cell, wherein the radiant cell forms an exhaust gas; contacting the exhaust gas with the convective bank to heat the first portion of the hydrocarbon stream; monitoring a temperature of the first portion of the hydrocarbon stream; and adjusting the ratio to change an amount of the first portion flowing to the convective bank when the temperature of the first portion of the hydrocarbon stream exceeds a maximum value. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph further comprising reacting the effluent in a second reaction zone to form a second effluent; heating the second effluent in a second radiant cell, wherein the second radiant cell forms a second exhaust gas; contacting the second exhaust gas with the convective bank to heat the first portion of the hydrocarbon stream; reacting the second effluent in a third reaction zone to form a third effluent; heating the third effluent in a third radiant cell, wherein the third radiant cell forms a third exhaust gas; contacting the third exhaust gas with the convective bank to heat the first portion of the hydrocarbon stream; and reacting the third effluent in a fourth reaction zone to form a product effluent. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph further comprising passing the product effluent through a heat exchanger; and heating the hydrocarbon stream in the heat exchanger before dividing the hydrocarbon stream into a first portion and a second portion according to a ratio. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph further comprising condensing the product effluent to form a product stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph further comprising passing the second portion of the hydrocarbon feed through a valve before adding the second portion of the hydrocarbon stream to the effluent, and wherein adjusting the ratio to change the amount of the first portion flowing to the convective bank comprises closing the valve. An

embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein monitoring a temperature of the first portion of the hydrocarbon stream comprises monitoring a temperature of the first portion of the hydrocarbon stream exiting the convective bank.

[0054] A third embodiment of the invention is an apparatus for processing a hydrocarbon stream, the apparatus comprising a heat exchanger configured to heat the hydrocarbon stream; a convective bank configured to receive a first portion of the hydrocarbon stream; a reaction zone configured to receive the first portion from the convective bank and to react the first portion in a reaction zone to form an effluent; a radiant cell configured to receive and heat the effluent and a second portion of the hydrocarbon stream, wherein the radiant cell forms an exhaust gas, and wherein the radiant cell is configured to pass the exhaust gas to the convective bank to heat the first portion of the hydrocarbon stream; a temperature sensor configured to monitor a temperature of the first portion exiting the convective bank; and a flow controller configured to change an amount of the first portion flowing to the convective bank in response to the temperature of the first portion exiting the convective bank.

[0055] Without further elaboration, it is believed that using the preceding description that one skilled in the art can utilize the present invention to its fullest extent and easily ascertain the essential characteristics of this invention, without departing from the spirit and scope thereof, to make various changes and modifications of the invention and to adapt it to various usages and conditions. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limiting the remainder of the disclosure in any way whatsoever, and that it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

[0056] In the foregoing, all temperatures are set forth in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.

WHAT IS CLAIMED IS:

1. A method for processing a hydrocarbon stream, the method comprising the steps of:

heating a feed stream in a convective bank;
reacting the feed stream in a first reaction zone to form a first effluent;
heating the first effluent in a first radiant cell, wherein the first radiant cell combusts fuel gas to heat the first effluent and forms a first exhaust gas; and
contacting the first exhaust gas with the convective bank to heat the feed stream.

2. The method of claim 1 further comprising dividing the feed stream into a first portion and a second portion, wherein heating a feed stream in a convective bank comprises heating the first portion of the feed stream in a convective bank, wherein reacting the feed stream in a first reaction zone to form a first effluent comprises reacting the first portion of the feed stream in a first reaction zone to form a first effluent, and wherein the method further comprises mixing the second portion of the feed stream with the first effluent before heating the first effluent in a first radiant cell.

3. The method of claim 2 wherein dividing the feed stream into a first portion and a second portion comprises:

monitoring a temperature of the feed stream exiting the convective bank; and
selectively increasing an amount of the first portion of the feed stream flowing to the convective bank in response to the temperature of the feed stream exiting the convective bank.

4. The method of claim 2 wherein the first reaction zone has a required inlet temperature and wherein dividing the feed stream into a first portion and a second portion comprises:

monitoring a temperature of the feed stream exiting the convective bank to determine whether the temperature exceeds the required inlet temperature; and
selectively increasing an amount of the first portion of the feed stream flowing to the convective bank if the temperature exceeds the required inlet temperature.

5. The method of claim 1 wherein the convective bank comprises shock tube rows and/or finned tube rows, and wherein heating the feed stream in a convective bank comprises heating the feed stream in the shock tube rows and/or in the finned tube rows.

6. The method of claim 1 further comprising adding a recycled gas stream comprising hydrogen to the feed stream before heating the feed stream in the convective bank.

7. The method of claim 1 further comprising:
reacting the first effluent in a second reaction zone to form a second effluent;
heating the second effluent in a second radiant cell, wherein the second radiant cell combusts fuel gas to heat the second effluent and forms a second exhaust gas;
contacting the second exhaust gas with the convective bank to heat the feed stream;
reacting the second effluent in a third reaction zone to form a third effluent;
heating the third effluent in a third radiant cell, wherein the third radiant cell combusts fuel gas to heat the third effluent and forms a third exhaust gas;
contacting the third exhaust gas with the convective bank to heat the feed stream;
and
reacting the third effluent in a fourth reaction zone to form a product effluent.

8. The method of claim 7 further comprising dividing the feed stream into a first portion and a second portion, wherein heating the feed stream in a convective bank comprises heating the first portion of the feed stream in a convective bank, wherein reacting the feed stream in a first reaction zone to form a first effluent comprises reacting the first portion of the feed stream in a first reaction zone to form a first effluent, and wherein the method further comprises mixing the second portion of the feed stream with the first effluent before heating the first effluent in a first radiant cell.

9. The method of claim 7 further comprising:
passing the product effluent through a heat exchanger; and
heating the feed stream in the heat exchanger before heating the feed stream in the convective bank.

10. The method of claim 7 further comprising dividing the feed stream into a first portion and a second portion, wherein heating a feed stream in a convective bank comprises heating the first portion of the feed stream in a convective bank, wherein reacting the feed stream in a first reaction zone to form a first effluent comprises reacting the first portion of the feed stream in a first reaction zone to form a first effluent, and wherein the method further comprises mixing the second portion of the feed stream with the first effluent before heating the first effluent in a first radiant cell.

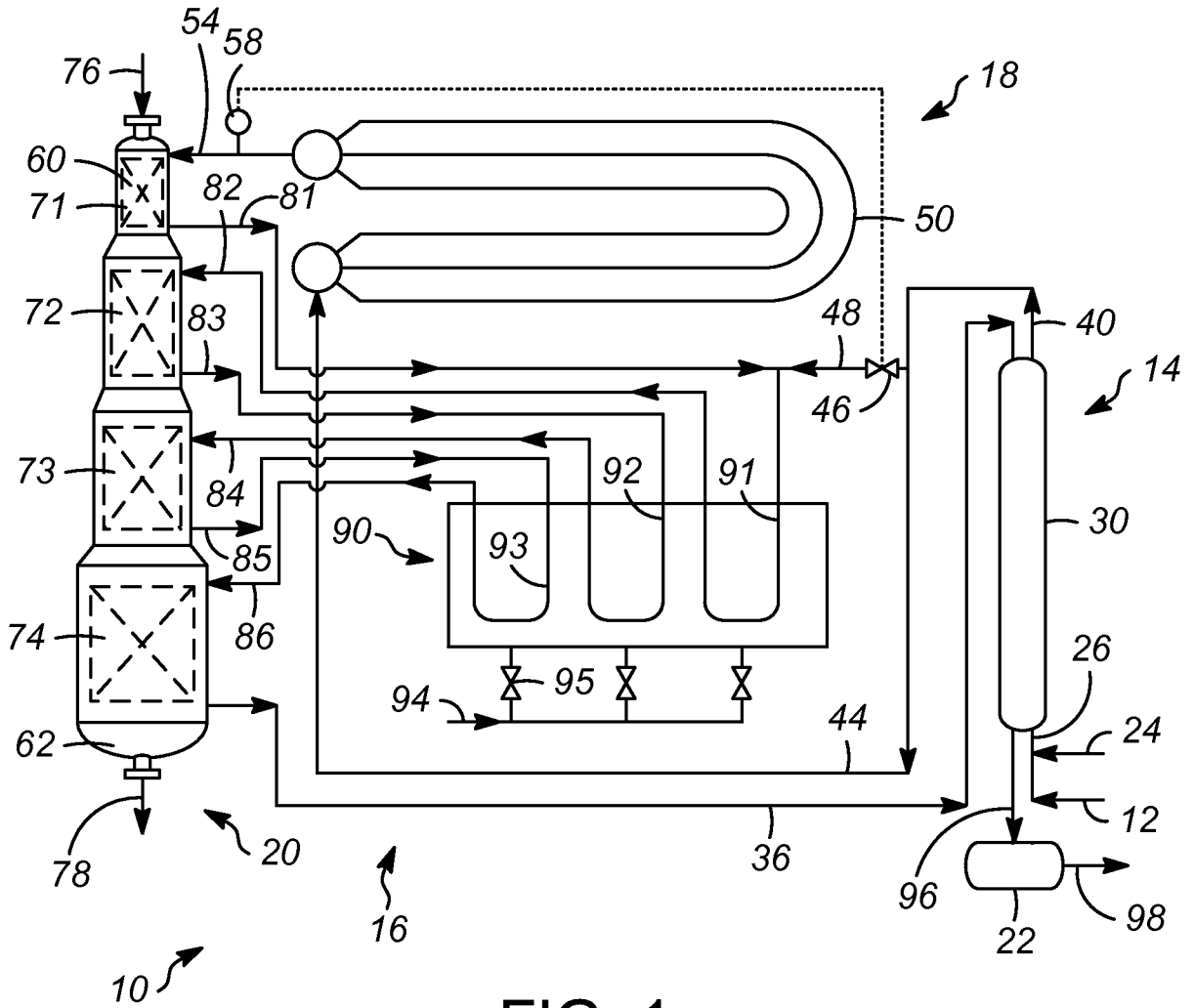


FIG. 1

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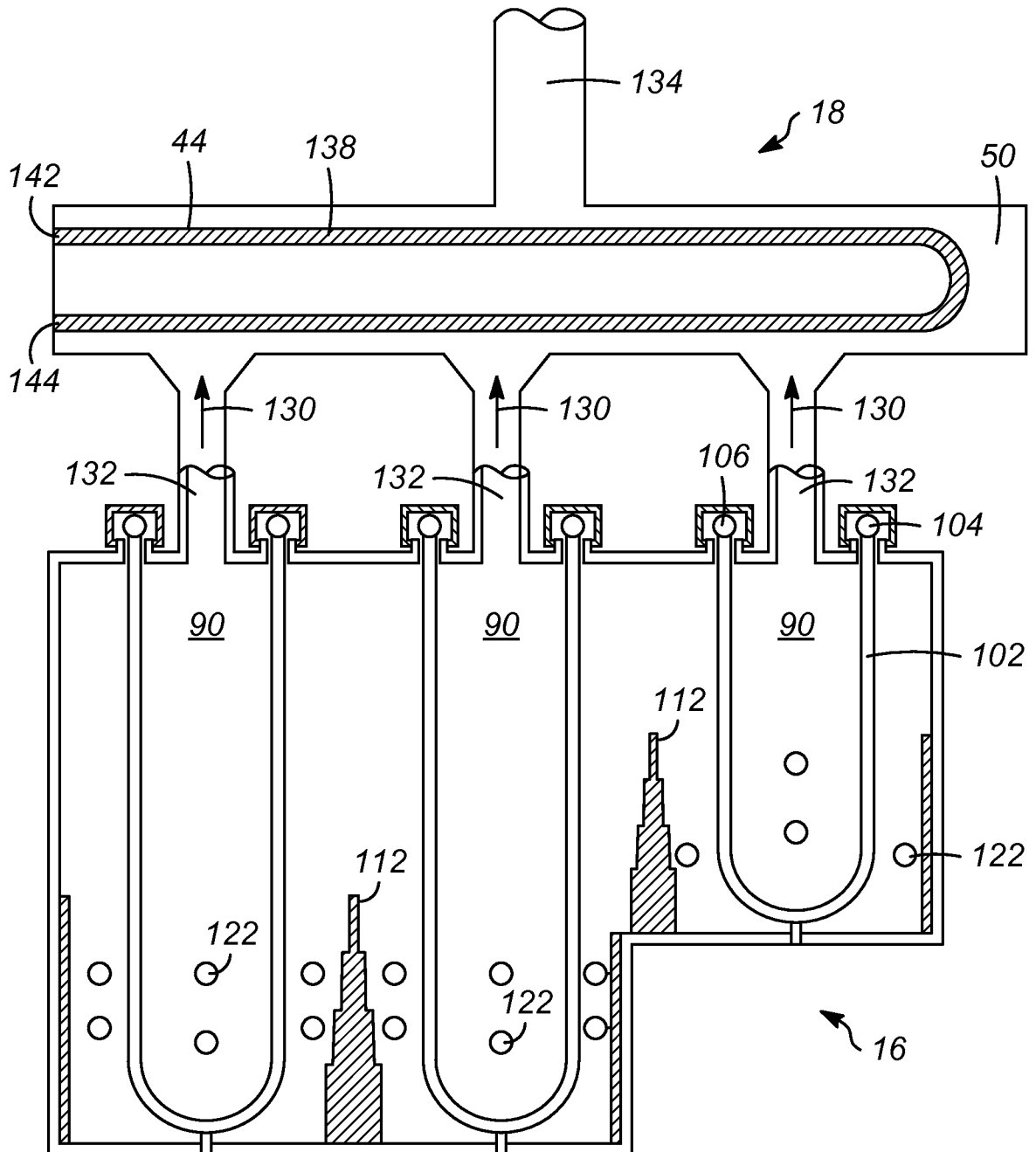


FIG. 2

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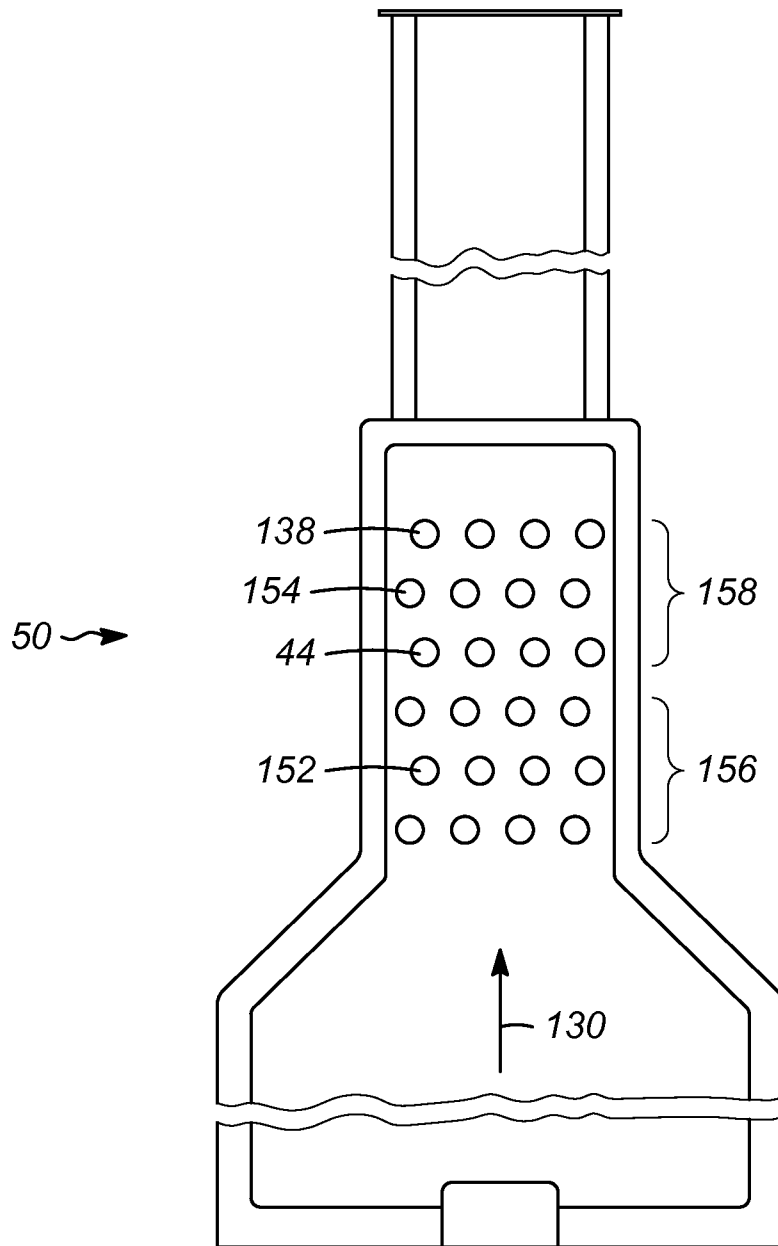


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/031821**A. CLASSIFICATION OF SUBJECT MATTER****C10G 9/36(2006.01)i**

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

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
C10G 9/36; C10G 69/08; C10G 51/06; C10G 25/00; C10G 9/14; C10G 35/04; F28D 1/00; C10G 9/20Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility modelsElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: hydrocarbon, heating, convective bank, radiant cell, fuel gas, exhaust gas**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2008-0110801 A1 (YUAN, L. et al.) 15 May 2008 See abstract; paragraphs [0007], [0031], [0032], [0051], [0053], [0054], [0057], [0059], [0063] - [0068], [0076]; claim 1; and figures 1 - 4.	1-10
A	US 2004-0089588 A1 (GARG, A.) 13 May 2004 See abstract; paragraph [0022]; claim 1; and figure 3.	1-10
A	US 5879537 A (PETERS, K. D.) 09 March 1999 See abstract; column 3, line 52 - column 4, line 39, column 6, lines 41 - 52, column 8, line 57 - column 9, line 45; claim 1; and figure 1.	1-10
A	US 5976354 A (POWERS, J. R. et al.) 02 November 1999 See column 11, line 43 - column 12, line 3; and figure 2.	1-10
A	US 4792436 A (TSAI, F. W.) 20 December 1988 See abstract; column 1, lines 46 - 66, column 2, line 58 - column 3, line 9, column 4, lines 46 - 58; claim 1; and figures 1, 2, 12.	1-10

 Further documents are listed in the continuation of Box C. 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

08 July 2014 (08.07.2014)

Date of mailing of the international search report

10 July 2014 (10.07.2014)

Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2014/031821

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2008-0110801 A1	15/05/2008	AR 063617 A1 TW 200835784 A WO 2008-060848 A2 WO 2008-060848 A3	04/02/2009 01/09/2008 22/05/2008 31/07/2008
US 2004-0089588 A1	13/05/2004	US 7204966 B2	17/04/2007
US 5879537 A	09/03/1999	CA 2264498 A1 CA 2264498 C CN 1200914 C CN 1266038 A DE 69932314 D1 DE 69932314 T2 EP 1033398 A1 EP 1033398 B1 JP 04018835 B2 JP 2000-256673 A TW 499473 A US 5879537 A	04/09/2000 22/09/2009 11/05/2005 13/09/2000 24/08/2006 05/07/2007 06/09/2000 12/07/2006 05/12/2007 19/09/2000 21/08/2002 09/03/1999
US 5976354 A	02/11/1999	None	
US 4792436 A	20/12/1988	US 879020 A	07/11/1989