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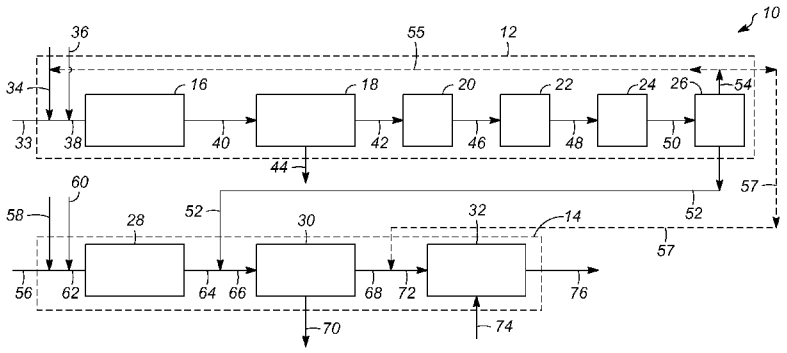


FIG. 1

(57) **Abstract**: Embodiments of methods and apparatuses for isomerization of paraffins are provided. In one example, a method comprises the steps of compressing a C_4- hydrocarbons-containing stabilizer vapor stream to form a compressed C_4- hydrocarbons-containing stabilizer stream. A C_4 hydrocarbons-containing feed stream that comprises unbranched C_4 hydrocarbons is contacted with a chloride-promoted isomerization catalyst in the presence of hydrogen to form a branched C_4 hydrocarbons-containing reaction zone effluent. At least a portion of the compressed C_4- hydrocarbons-containing stabilizer stream is combined with the branched C_4 hydrocarbons-containing reaction zone effluent to form a C_4 hydrocarbons-containing combined stream. The C_4 hydrocarbons-containing combined stream is separated into a C_3- hydrocarbons-containing stabilizer vapor stream and a C_4 hydrocarbons-rich product stream that comprises branched C_4 hydrocarbons.

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METHODS AND APPARATUSES FOR ISOMERIZATION OF PARAFFINS

STATEMENT OF PRIORITY

[0001] This application claims priority to U.S Application No. 13/672,256 which was filed November 8, 2012, the contents of which are hereby incorporated by reference in its entirety.

TECHNICAL FIELD

[0002] The technical field relates generally to methods and apparatuses for isomerization of hydrocarbons, and more particularly relates to methods and apparatuses for isomerization of paraffins with recovery of C_4 hydrocarbons.

BACKGROUND

[0003] Isomerization processes are widely used by many refiners to rearrange the molecular structure of straight chain paraffinic hydrocarbons to more highly branched hydrocarbons. Generally, these more highly branched hydrocarbons have relatively high octane ratings.

[0004] Paraffin feeds for C_5/C_6 hydrocarbons isomerization processes can contain cyclic C_6^+ hydrocarbons such as benzene and cyclic C_7^+ hydrocarbons. As used herein, C_x hydrocarbons means hydrocarbon molecules that have "X" number of carbon atoms, C_x^+ hydrocarbons means hydrocarbon molecules that have "X" and more than "X" number of carbon atoms, and C_x^- hydrocarbons means hydrocarbon molecules that have "X" and less than "X" number of carbon atoms. As used herein, C_5/C_6 hydrocarbons mean C_5 hydrocarbons and/or C_6 hydrocarbons. When the weight percent of cyclic C_6^+ hydrocarbons in the paraffin feed is 20% or greater (also referred to as an X-factor of 20 or greater in which the X-factor is defined as the sum of the weight percent of the cyclic C_6 hydrocarbons plus C_7^+ hydrocarbons in the feed, e.g., benzene + cyclohexane + methylcyclopentane + C_7^+), the paraffin feed is considered a "hard feed to isomerize." In particular, the C_7^+ hydrocarbons and to a much lesser extent C_5 and C_6 hydrocarbons in the reactor tend to hydrocrack, producing C_4 hydrocarbons as well as other lighter hydrocarbons, e.g., C_3^- hydrocarbons. The C_4 hydrocarbons have significant caloric and economic value. Unfortunately, the C_4 hydrocarbons are traditionally removed in an off-

gas stream of C_5/C_6 hydrocarbons isomerization processes and burned because the investment and operating costs for recovering the C_4 hydrocarbons are prohibitively expensive.

[0005] Accordingly, it is desirable to provide methods and apparatuses for isomerization of paraffins including recovery of C_4 hydrocarbons with reduced overall investment and/or operating costs. Moreover, it is desirable to provide methods and apparatuses for isomerization of paraffins including recovery of C_4 hydrocarbons, such as for C_5/C_6 hydrocarbons isomerization processes that have paraffinic feed streams that may contain some C_7^+ hydrocarbons. Furthermore, other desirable features and characteristics of the present invention will become apparent from the subsequent detailed description and the appended claims, taken in conjunction with the accompanying drawings and this background.

BRIEF SUMMARY

[0006] Methods and apparatuses for isomerization of paraffins are provided herein. In accordance with an exemplary embodiment, a method for isomerization of paraffins comprises the steps of compressing a C_4^- hydrocarbons-containing stabilizer vapor stream to form a compressed C_4^- hydrocarbons-containing stabilizer stream. A C_4 hydrocarbons-containing feed stream that comprises unbranched C_4 hydrocarbons is contacted with a chloride-promoted isomerization catalyst in the presence of hydrogen to form a branched C_4 hydrocarbons-containing reaction zone effluent. At least a portion of the compressed C_4^- hydrocarbons-containing stabilizer stream is combined with the branched C_4 hydrocarbons-containing reaction zone effluent to form a C_4 hydrocarbons-containing combined stream. The C_4 hydrocarbons-containing combined stream is separated into a C_3^- hydrocarbons-containing stabilizer vapor stream and a C_4 hydrocarbons-rich product stream that comprises branched C_4 hydrocarbons.

[0007] In accordance with another exemplary embodiment, a method for isomerization of paraffins is provided. The method comprises the steps of contacting a C_5^+ hydrocarbons-containing feed stream that comprises unbranched C_5/C_6 hydrocarbons with a chloride-promoted isomerization catalyst in the presence of hydrogen to form a branched C_5^+ hydrocarbons-containing reaction zone effluent. The branched C_5^+ hydrocarbons-containing reaction zone effluent is separated into a C_4^- hydrocarbons-containing stabilizer vapor stream and a C_5^+ hydrocarbon-rich product stream that comprises branched C_5^+

hydrocarbons. The C_4^- hydrocarbons-containing stabilizer vapor stream is compressed to form a compressed C_4^- hydrocarbons-containing stabilizer stream. The compressed C_4^- hydrocarbons-containing stabilizer stream is cooled to form a cooled, compressed C_4^- hydrocarbons-containing stabilizer stream. The cooled, compressed C_4^- hydrocarbons-containing stabilizer stream is separated into a C_4 hydrocarbons-containing liquid stream and a C_3^- hydrocarbons-containing off gas stream. The C_4 hydrocarbons-containing liquid stream is combined with a branched C_4 hydrocarbons-containing reaction zone effluent to form a C_4 hydrocarbons-containing combined stream. The C_4 hydrocarbons-containing combined stream is separated into a C_3^- hydrocarbons-containing stabilizer vapor stream and a C_4 hydrocarbons-rich product stream that comprises branched C_4 hydrocarbons.

[0008] In accordance with another exemplary embodiment, an apparatus for isomerization of paraffins is provided. The apparatus comprises a compressor that is configured to receive and compress a C_4^- hydrocarbons-containing stabilizer vapor stream to form a compressed C_4^- hydrocarbons-containing stabilizer stream. A reaction zone contains a chloride-promoted isomerization catalyst in the presence of hydrogen. The reaction zone is configured to receive a C_4 hydrocarbons-containing feed stream that comprises unbranched C_4 hydrocarbons and to operate at isomerization conditions effective to form a branched C_4 hydrocarbons-containing reaction zone effluent. The apparatus is configured to combine at least a portion of the compressed C_4^- hydrocarbons-containing stabilizer stream and the branched C_4 hydrocarbons-containing reaction zone effluent to form a C_4 hydrocarbons-containing combined stream. A stabilizer zone is configured to receive and separate the C_4 hydrocarbons-containing combined stream into a C_3^- hydrocarbons-containing stabilizer vapor stream and a C_4 hydrocarbons-rich product stream that comprises branched C_4 hydrocarbons.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The various embodiments will hereinafter be described in conjunction with the following drawing figures, wherein like numerals denote like elements, and wherein:

[0010] FIG. 1 schematically illustrates an apparatus and method for isomerization of paraffins in accordance with an exemplary embodiment; and

[0011] FIG. 2 schematically illustrates an apparatus and method for isomerization of paraffins in accordance with another exemplary embodiment.

DETAILED DESCRIPTION

[0012] The following detailed description is merely exemplary in nature and is not intended to limit the various embodiments or the application and uses thereof. Furthermore, there is no intention to be bound by any theory presented in the preceding background or the following detailed description.

[0013] Various embodiments contemplated herein relate to methods and apparatuses for isomerization of paraffins. Unlike the prior art, the exemplary embodiments of the apparatus taught herein integrate a C_5/C_6 hydrocarbons isomerization section with a C_4 hydrocarbons isomerization section. In the C_5/C_6 hydrocarbons isomerization section, a C_5^+ hydrocarbons-containing feed stream that comprises unbranched C_5/C_6 hydrocarbons is contacted with a chloride-promoted isomerization catalyst in the presence of hydrogen in a first reaction zone to form a branched C_5^+ hydrocarbons-containing reaction zone effluent. As used herein, the term "zone" refers to an area including one or more equipment items and/or one or more sub-zones. Equipment items can include one or more reactors or reactor vessels, heaters, exchangers, dryers, pipes, pumps, compressors, and controllers. Additionally, an equipment item, such as a reactor, dryer, or vessel, can further include one or more zones or sub-zones.

[0014] In an exemplary embodiment, the branched C_5^+ hydrocarbons-containing reaction zone effluent is introduced to a first stabilizer zone and separated into a C_4^- hydrocarbons-containing stabilizer vapor stream and a C_5^+ hydrocarbon-rich product stream that comprises branched C_5^+ hydrocarbons. The C_4^- hydrocarbons-containing stabilizer vapor stream comprises C_4 hydrocarbons, C_3^- hydrocarbons, hydrogen, and HCl. The C_4^- hydrocarbons-containing stabilizer vapor stream is compressed to form a compressed C_4^- hydrocarbons-containing stabilizer stream.

[0015] In the C_4 hydrocarbons isomerization section, a C_4 hydrocarbons-containing feed stream that comprises unbranched C_4 hydrocarbons is contacted with a chloride-promoted isomerization catalyst in the presence of hydrogen in a second reaction zone to form a branched C_4 hydrocarbons-containing reaction zone effluent. In an exemplary embodiment, at least a portion of the compressed C_4^- hydrocarbons-containing stabilizer stream from the C_5/C_6 hydrocarbons isomerization section is introduced to and combined with the branched C_4 hydrocarbons-containing reaction zone effluent to form a C_4 hydrocarbons-containing combined stream. The C_4 hydrocarbons-containing combined

stream is separated in a second stabilizer into a C_3^- hydrocarbons-containing stabilizer vapor stream and a C_4 hydrocarbons-rich product stream. In an exemplary embodiment, the C_4 hydrocarbons-rich product stream contains both branched and unbranched C_4 hydrocarbons correspondingly from the C_4 hydrocarbons isomerization section and the C_5/C_6 hydrocarbons isomerization section. The C_3^- hydrocarbons-containing stabilizer vapor stream comprises C_3^- hydrocarbons, hydrogen, and HCl. In an exemplary embodiment, the C_3^- hydrocarbons-containing stabilizer vapor stream is introduced to a scrubbing zone and is scrubbed with a caustic to neutralize HCl. The neutralized C_3^- hydrocarbons-containing stabilizer vapor stream is removed and may be burned as fuel gas.

[0016] Currently, some refiners employ separate isomerization processes for their operations, one for C_5/C_6 hydrocarbons isomerization and another for C_4 hydrocarbons isomerization. These isomerization processes often utilize correspondingly similar but independent equipment items, such as equipment for the scrubbing zones, which can have significant investment and operational cost. By integrating the C_5/C_6 hydrocarbons isomerization section with the C_4 hydrocarbons isomerization section in accordance with the various embodiments described herein, the C_4 hydrocarbons in the C_4^- hydrocarbons-containing stabilizer vapor stream from the C_5/C_6 hydrocarbons isomerization section can be recovered in the C_4 hydrocarbons isomerization section. Additionally, in an exemplary embodiment, the single scrubbing zone in the C_4 hydrocarbons isomerization section can be used to neutralize HCl from both the C_5/C_6 hydrocarbons isomerization section and the C_4 hydrocarbons isomerization section, thereby eliminating a separate scrubbing zone for the C_5/C_6 hydrocarbons isomerization process. As such, the total investment and operating costs for the isomerization process can be reduced compared to the total investment and operating costs for two separate isomerization processes, one for C_5/C_6 hydrocarbons isomerization and another for C_4 hydrocarbons isomerization.

[0017] Referring to FIG. 1, a schematic depiction of an apparatus 10 for isomerization of paraffins in accordance with an exemplary embodiment is provided. The apparatus 10 is utilized for a paraffin isomerization process that converts normal paraffins to branched paraffins. As illustrated, the apparatus 10 comprises a C_5/C_6 hydrocarbons isomerization section 12 and a C_4 hydrocarbons isomerization section 14 that is in fluid communication with the C_5/C_6 hydrocarbons isomerization section 12.

[0018] In an exemplary embodiment, the C_5/C_6 hydrocarbons isomerization section 12 comprises a reaction zone 16, a stabilizer zone 18, a compression suction drum 20, a compressor 22, a cooler 24, and a separator 26 that are in fluid communication. The C_4 hydrocarbons isomerization section 14 comprises a reaction zone 28, a stabilizer zone 30, and a scrubbing zone 32 that are in fluid communication.

[0019] A C_5^+ hydrocarbons-containing feed stream 33 is introduced to the C_5/C_6 hydrocarbons isomerization section 12. The C_5^+ hydrocarbons-containing feed stream 33 comprises normal or unbranched paraffinic C_5/C_6 hydrocarbons, such as normal pentane and normal hexane. In an exemplary embodiment, the C_5^+ hydrocarbons-containing feed stream 33 is relatively rich in C_5/C_6 hydrocarbons and further comprises cyclic C_6^+ and C_7^+ hydrocarbons. In one example, the C_5^+ hydrocarbons-containing feed stream 33 comprises the cyclic C_6^+ and C_7^+ hydrocarbons in an amount of 10 weight percent (wt. %) or greater, such as from 10 to 50 wt. % or greater, for example from 20 to 30 wt. %, of the C_5^+ hydrocarbons-containing feed stream 33. As such, the C_5^+ hydrocarbons-containing feed stream 33 is considered a feed stream that is "hard to isomerize," which can result in some hydrocracking of the cyclic C_6^+ and C_7^+ hydrocarbons during the isomerization of the C_5/C_6 hydrocarbons, thereby producing C_4^- hydrocarbons.

[0020] A hydrogen-containing gas feed 34 and a chloride promoter stream 36 (e.g., containing perchloroethylene or the like) are introduced to the C_5^+ hydrocarbons-containing feed stream 33 to form a combined stream 38. Although not illustrated, the C_5^+ hydrocarbons-containing feed stream 33, the hydrogen-containing gas feed 34, the chloride promoter stream 36, and/or the combined stream 38 may be passed through a dryer(s), a heat exchanger(s), and/or a heater(s) so that the combined stream 38 is dry and heated while advancing through the reaction zone 16. In an exemplary embodiment, the combined stream 38 is at a temperature of 90 to 210°C in the reaction zone 16.

[0021] In an exemplary embodiment, the reaction zone 16 comprises a fixed-bed catalytic reactor operating at a temperature of from 90 to 210°C and contains an isomerization catalyst that is activated by HCl by the decomposition of chloride promoter from the chloride promoter stream 36 to form a high-activity chloride-promoted isomerization catalyst. Non-limiting examples of the isomerization catalyst include alumina catalyst, platinum aluminum catalyst, and the like that can be chlorinated. The chloride-promoted isomerization catalyst in the presence of hydrogen is effective to

isomerize the normal paraffins to branched paraffins (e.g., branched pentane and/or branched hexane) to produce a branched C_5^+ hydrocarbons-containing reaction zone effluent 40. The branched C_5^+ hydrocarbons-containing reaction zone effluent 40 contains branched and some unbranched C_5/C_6 hydrocarbons, C_4 hydrocarbons, C_3^- hydrocarbons, some naphthenes and C_7 paraffins, hydrogen (e.g., unreacted hydrogen), HCl, and possibly other chloride-containing compounds.

[0022] The branched C_5^+ hydrocarbons-containing reaction zone effluent 40 is passed along to the stabilizer zone 18 and is separated at separation conditions into a C_4^- hydrocarbons-containing stabilizer vapor stream 42 and a C_5^+ hydrocarbon-rich product stream 44. In an exemplary embodiment, the stabilizer zone 18 (e.g., stabilizer overhead receiver) is operating at a temperature of from 30 to 45°C and a pressure of from 1030 to 1720 kPa gauge. In an exemplary embodiment, the C_4^- hydrocarbons-containing stabilizer vapor stream 42 comprises C_4 hydrocarbons, C_3^- hydrocarbons, hydrogen, and HCl. The C_5^+ hydrocarbon-rich product stream 44 is rich in branched C_5^+ hydrocarbons (e.g., C_5/C_6 hydrocarbons), such as branched pentanes and/or branched hexanes, and is removed from the apparatus 10 as product.

[0023] As illustrated, the C_4^- hydrocarbons-containing stabilizer vapor stream 42 is passed through the compression suction drum 20 to remove mist droplets and/or deposits from the vapor stream 42 and to form a demisted, C_4^- hydrocarbons-containing stabilizer vapor stream 46. In an exemplary embodiment, the demisted, C_4^- hydrocarbons-containing stabilizer vapor stream 46 is introduced to the compressor 22 at a temperature of from 30 to 45°C and a pressure of from 1030 to 1720 kPa gauge. The compressor 22 compresses the demisted, C_4^- hydrocarbons-containing stabilizer vapor stream 46 to form a compressed C_4^- hydrocarbons-containing stabilizer stream 48. In an exemplary embodiment, the compressor 22 pressurizes the vapor stream 46 to forms the compressed C_4^- hydrocarbons-containing stabilizer stream 48 having a pressure of from 2760 to 4210 kPa gauge and a temperature of from 70 to 120°C.

[0024] As illustrated, the compressed C_4^- hydrocarbons-containing stabilizer stream 48 is passed along to the cooler 24, which cools the compressed C_4^- hydrocarbons-containing stabilizer stream 48 to form a cooled, compressed C_4^- hydrocarbons-containing stabilizer stream 50. In an exemplary embodiment, the cooled, compressed C_4^- hydrocarbons-containing stabilizer stream 50 has a temperature of from 0 to 45°C, such as from 30 to

45°C, and a pressure of from 2660 to 4140 kPa gauge. The cooled, compressed C_4^- hydrocarbons-containing stabilizer stream 50 is separated in the separator 26 to form a C_4 hydrocarbons-containing liquid stream 52 and a C_3^- hydrocarbons-containing off gas stream 54. In an exemplary embodiment, the C_4 hydrocarbons-containing liquid stream 52 is rich in C_4 hydrocarbons, e.g., branched and/or unbranched paraffinic C_4 hydrocarbons, a significant portion of which were formed in the reaction zone 16 due to hydrocracking of C_7^+ hydrocarbons contained in the C_5^+ hydrocarbons-containing feed stream 33. The C_3^- hydrocarbons-containing off gas stream 54 comprises C_3^- hydrocarbons, hydrogen, and HCl.

[0025] The C_3^- hydrocarbons-containing off gas stream 54 may be divided into portions 55 and 57. In an exemplary embodiment, at least the portion 55 of the C_3^- hydrocarbons-containing off gas stream 54 is recycled back to the C_5^+ hydrocarbons-containing feed stream 33, e.g., via direct introduction to stream 33, 34, or 38, for introduction to the reaction zone 16. As illustrated, the portion 55 of the C_3^- hydrocarbons-containing off gas stream 54 is introduced to the hydrogen-containing gas feed 34, which is introduced to the C_5^+ hydrocarbons-containing feed stream 33 to form the combined stream 38. As such, HCl and hydrogen contained in the portion 55 of the C_3^- hydrocarbons-containing off gas stream 54 helped to replenish hydrogen and chloride promoter consumed during the isomerization reaction, thereby reducing the amount of makeup hydrogen and chloride promoter needed from the hydrogen-containing gas feed 34 and the chloride promoter stream 36, respectively. In an exemplary embodiment, at least the portion 57 of the C_3^- hydrocarbons-containing off gas stream 54 is passed along to the C_4 hydrocarbons isomerization section 14 for further processing and to neutralize HCl in the off gas stream 54 as discussed in further detail below. In an exemplary embodiment and as illustrated, at least a portion 57' of the portion 57 of the C_3^- hydrocarbons-containing off gas stream 54 is introduced to the stream 58 and/or 62 to help replenish hydrogen and chloride promoter consumed during the isomerization reaction, thereby reducing the amount of makeup hydrogen and/or chloride promoter needed from the hydrogen-containing gas feed 58 and/or the chloride promoter stream 60, respectively. In an exemplary embodiment, C_3^- hydrocarbons-containing off gas stream 54 is divided such that portion 55 corresponds to 30 to 70%, such as from 40 to 60%, of the mass flow rate of the C_3^- hydrocarbons-containing off gas stream 54 and the portion 57 corresponds to 30 to 70%, such as from 40

to 60%, of the mass flow rate of the off gas stream 54. In this embodiment, the ratio of the portion 55 to the portion 57 is such that the C_5/C_6 hydrocarbons isomerization section 12 maintains a suitable material balance that is not overly weighted with light end hydrocarbons, e.g., C_3^- hydrocarbons.

[0026] The C_4 hydrocarbons-containing liquid stream 52 is passed along to the C_4 hydrocarbons isomerization section 14 downstream from the reaction zone 28. Upstream from the reaction zone 28, a C_4 hydrocarbons-containing feed stream 56 is introduced to the C_4 hydrocarbons isomerization section 14. The C_4 hydrocarbons-containing feed stream 56 comprises normal or unbranched paraffinic C_4 hydrocarbons, such as normal butane. A hydrogen-containing gas feed 58 and a chloride promoter stream 60 (e.g., containing perchloroethylene or the like) are introduced to the C_4 hydrocarbons-containing feed stream 56 to form a combined stream 62. Although not illustrated, the C_4 hydrocarbons-containing feed stream 56, the hydrogen-containing gas stream 58, the chloride promoter stream 60, and/or the combined stream 62 may be passed through a dryer(s), a heat exchanger(s), and/or a heater(s) so that the combined stream 62 is dry and heated while advancing through the reaction zone 28. In an exemplary embodiment, the combined stream 38 is at a temperature of 90 to 210°C in the reaction zone 16.

[0027] In an exemplary embodiment, the reaction zone 28 comprises a fixed-bed catalytic reactor operating at a temperature of from 90 to 210°C and contains an isomerization catalyst that is activated by HCl by the decomposition of chloride promoter from the chloride promoter stream 60 to form a high-activity chloride-promoted isomerization catalyst as described above in relation to the reaction zone 16. The chloride-promoted isomerization catalyst in the presence of hydrogen is effective to isomerize the normal paraffins to branched paraffins (e.g., branched butane) to produce a branched C_4 hydrocarbons-containing reaction zone effluent 64. The branched C_4 hydrocarbons-containing reaction zone effluent 64 contains branched and unbranched C_4 hydrocarbons, C_3^- hydrocarbons, hydrogen (e.g., unreacted hydrogen), HCl, and possibly other chloride-containing compounds and other hydrocarbons such as C_5 hydrocarbons and some trace C_6^+ hydrocarbons.

[0028] In an exemplary embodiment, the C_4 hydrocarbons-containing liquid stream 52 is combined with the branched C_4 hydrocarbons-containing reaction zone effluent 64 to form a C_4 hydrocarbons-containing combined stream 66. In an exemplary embodiment, the C_4

hydrocarbons-containing combined stream 66 has a pressure of from 2000 to 2760 kPa gauge and a temperature of from 30 to 150°C, such as from 80 to 110°C. The C_4 hydrocarbons-containing combined stream 66 is passed through the stabilizer zone 30 and separated into a C_3^- hydrocarbons-containing stabilizer vapor stream 68 and a C_4 hydrocarbons-rich product stream 70. The C_4 hydrocarbons-rich product stream 70 is rich in C_4 hydrocarbons including branched C_4 hydrocarbons, such as branched butane or isobutane, and is removed from the apparatus 10 as product. The C_3^- hydrocarbons-containing stabilizer vapor stream 68 comprises C_3^- hydrocarbons, hydrogen, and HCl. In an exemplary embodiment, the C_3^- hydrocarbons-containing stabilizer vapor stream 68 has a pressure of from 1000 to 2410 kPa gauge, such as from 1720 to 2410 kPa gauge, and a temperature of from 0 (or lower, e.g., -40°C) to 45°C.

[0029] In an exemplary embodiment, at least the portion 57 of the C_3^- hydrocarbons-containing off gas stream 54 is combined with the C_3^- hydrocarbons-containing stabilizer vapor stream 68 to form a C_3^- hydrocarbons-containing combined stream 72. The C_3^- hydrocarbons-containing combined stream 72 comprises C_3^- hydrocarbons, hydrogen, and HCl. The C_3^- hydrocarbons-containing combined stream 72 is passed to the scrubbing zone 32. The scrubbing zone 32 scrubs the C_3^- hydrocarbons-containing combined stream 72 by neutralizing the HCl contained therein with a caustic 74, e.g., sodium hydroxide, to form a neutralized off gas stream 76 that is removed from the apparatus 10 and may be burned as fuel gas, for example.

[0030] Referring to FIG. 2, the apparatus 10 in accordance with another exemplary embodiment is provided. The apparatus 10 as shown in FIG. 2 is similarly configured to the apparatus 10 as shown in FIG. 1 and discussed above but without the cooler 24, the separator 26, and the resulting streams 50, 52, 54, 55, and 57. In this embodiment, the compressed C_4^- hydrocarbons-containing stabilizer stream 48 from the C_5/C_6 hydrocarbons isomerization section 12 is passed along to the C_4 hydrocarbons isomerization section 14 and combined with the branched C_4 hydrocarbons-containing reaction zone effluent 64 to form the C_4 hydrocarbons-containing combined stream 66. In an exemplary embodiment, the C_4 hydrocarbons-containing combined stream 66 has a pressure of from 2000 to 2760 kPa gauge and a temperature of from 30 to 150°C.

[0031] As discussed above, the C_4 hydrocarbons-containing combined stream 66 is separated in the stabilizer zone 30 into the C_3^- hydrocarbons-containing stabilizer vapor

stream 68 and the C_4 hydrocarbons-rich product stream 70. The C_4 hydrocarbons-rich product stream 70 is rich in C_4 hydrocarbons including branched C_4 hydrocarbons, such as branched butane or isobutane, and is removed from the apparatus 10 as product. The C_3^- hydrocarbons-containing stabilizer vapor stream 68 comprises C_3^- hydrocarbons, hydrogen, and HCl. In an exemplary embodiment, the C_3^- hydrocarbons-containing stabilizer vapor stream 68 has a pressure of from 1000 to 2410 kPa gauge, such as from 1720 to 2410 kPa gauge, and a temperature of from 0 (or lower, e.g., -40°C) to 45°C.

[0032] In an exemplary embodiment, the C_3^- hydrocarbons-containing stabilizer vapor stream 68 is passed to the scrubbing zone 32. The scrubbing zone 32 scrubs the C_3^- hydrocarbons-containing stabilizer vapor stream 68 by neutralizing the HCl contained therein with the caustic 74 to form the neutralized off gas stream 76 that is removed from the apparatus 10 and may be burned as fuel gas, for example.

[0033] Accordingly, methods and apparatuses for isomerization of paraffins have been described. The exemplary embodiments taught herein integrate a C_5/C_6 hydrocarbons isomerization section with a C_4 hydrocarbons isomerization section. By integrating the C_5/C_6 hydrocarbons isomerization section with the C_4 hydrocarbons isomerization section as described herein, C_4 hydrocarbons contained in a stabilizer vapor stream from the C_5/C_6 hydrocarbons isomerization section that would otherwise be burned as fuel gas can be recovered in the C_4 hydrocarbons isomerization section as part of a product stream.

[0034] While at least one exemplary embodiment has been presented in the foregoing detailed description of the disclosure, 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 disclosure 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 of the disclosure. 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 of the disclosure as set forth in the appended claims.

CLAIMS

What is claimed is:

1. A method for isomerization of paraffins, the method comprising the steps of:

compressing a C_4^- hydrocarbons-containing stabilizer vapor stream (42) to form a compressed C_4^- hydrocarbons-containing stabilizer stream (48);

contacting a C_4 hydrocarbons-containing feed stream (56) that comprises unbranched C_4 hydrocarbons with a chloride-promoted isomerization catalyst in the presence of hydrogen to form a branched C_4 hydrocarbons-containing reaction zone effluent (64);

combining at least a portion of the compressed C_4^- hydrocarbons-containing stabilizer stream (48) with the branched C_4 hydrocarbons-containing reaction zone effluent (64) to form a C_4 hydrocarbons-containing combined stream (66); and

separating the C_4 hydrocarbons-containing combined stream (66) into a C_3^- hydrocarbons-containing stabilizer vapor stream (68) and a C_4 hydrocarbons-rich product stream (70) that comprises branched C_4 hydrocarbons.

2. The method of claim 1, wherein the step of compressing comprises compressing the C_4^- hydrocarbons-containing stabilizer vapor stream (42) to a pressure of from 2760 to 4210 kPa gauge to form the compressed C_4^- hydrocarbons-containing stabilizer stream (48).

3. The method of claim 1, wherein the step of combining comprises forming the C_4 hydrocarbons-containing combined stream (66) having a pressure of from 2000 to 2760 kPa gauge.

4. The method of claim 1, wherein the step of combining comprises forming the C_4 hydrocarbons-containing combined stream (66) having a temperature of from 30 to 150°C.

5. The method of claim 1, wherein the step of separating comprises forming the C_3^- hydrocarbons-containing stabilizer vapor stream (68) having a pressure of from 1000 to 2410 kPa gauge.

6. The method of claim 1, wherein the step of separating comprises forming the C_3^- hydrocarbons-containing stabilizer vapor stream (68) having a temperature of from -40 to 45°C.

7. The method of claim 1, further comprising the step of:

demisting the C_4^- hydrocarbons-containing stabilizer vapor stream (42) to remove mist droplets and/or deposits from the C_4^- hydrocarbons-containing stabilizer vapor stream (42) prior to the step of compressing.

8. A method for isomerization of paraffins, the method comprising the steps of:

contacting a C_5^+ hydrocarbons-containing feed stream (33) that comprises unbranched C_5/C_6 hydrocarbons with a chloride-promoted isomerization catalyst in the presence of hydrogen to form a branched C_5^+ hydrocarbons-containing reaction zone effluent (40);

separating the branched C_5^+ hydrocarbons-containing reaction zone effluent (40) into a C_4^- hydrocarbons-containing stabilizer vapor stream (42) and a C_5^+ hydrocarbon-rich product stream (44) that comprises branched C_5^+ hydrocarbons;

compressing the C_4^- hydrocarbons-containing stabilizer vapor stream (42) to form a compressed C_4^- hydrocarbons-containing stabilizer stream (48);

cooling the compressed C_4^- hydrocarbons-containing stabilizer stream (48) to form a cooled, compressed C_4^- hydrocarbons-containing stabilizer stream (50); and

separating the cooled, compressed C_4^- hydrocarbons-containing stabilizer stream (50) into a C_4 hydrocarbons-containing liquid stream (52) and a C_3^- hydrocarbons-containing off gas stream (54);

combining the C_4 hydrocarbons-containing liquid stream (52) with a branched C_4 hydrocarbons-containing reaction zone effluent (64) to form a C_4 hydrocarbons-containing combined stream (66); and

separating the C_4 hydrocarbons-containing combined stream (66) into a C_3^- hydrocarbons-containing stabilizer vapor stream (68) and a C_4 hydrocarbons-rich product stream (70) that comprises branched C_4 hydrocarbons.

9. The method of claim 8, wherein the step of contacting comprises contacting the chloride-promoted isomerization catalyst with the C_5^+ hydrocarbons-containing feed stream (33) that further comprises cyclic C_6^+ and C_7^+ hydrocarbons.

10. An apparatus (10) for isomerization of paraffins, the apparatus (10) comprising:

a compressor (22) configured to receive and compress a C_4^- hydrocarbons-containing stabilizer vapor stream (42) to form a compressed C_4^- hydrocarbons-containing stabilizer stream (48);

a reaction zone (28) containing a chloride-promoted isomerization catalyst in the presence of hydrogen and configured to receive a C_4 hydrocarbons-containing feed stream (56) that comprises unbranched C_4 hydrocarbons and to operate at isomerization conditions effective to form a branched C_4 hydrocarbons-containing reaction zone effluent (64), wherein the apparatus (10) is configured to combine at least a portion of the compressed C_4^- hydrocarbons-containing stabilizer stream (48) and the branched C_4 hydrocarbons-containing reaction zone effluent (64) to form a C_4 hydrocarbons-containing combined stream (66); and

a stabilizer zone (30) configured to receive and separate the C_4 hydrocarbons-containing combined stream (66) into a C_3^- hydrocarbons-containing stabilizer vapor stream (68) and a C_4 hydrocarbons-rich product stream (70) that comprises branched C_4 hydrocarbons.

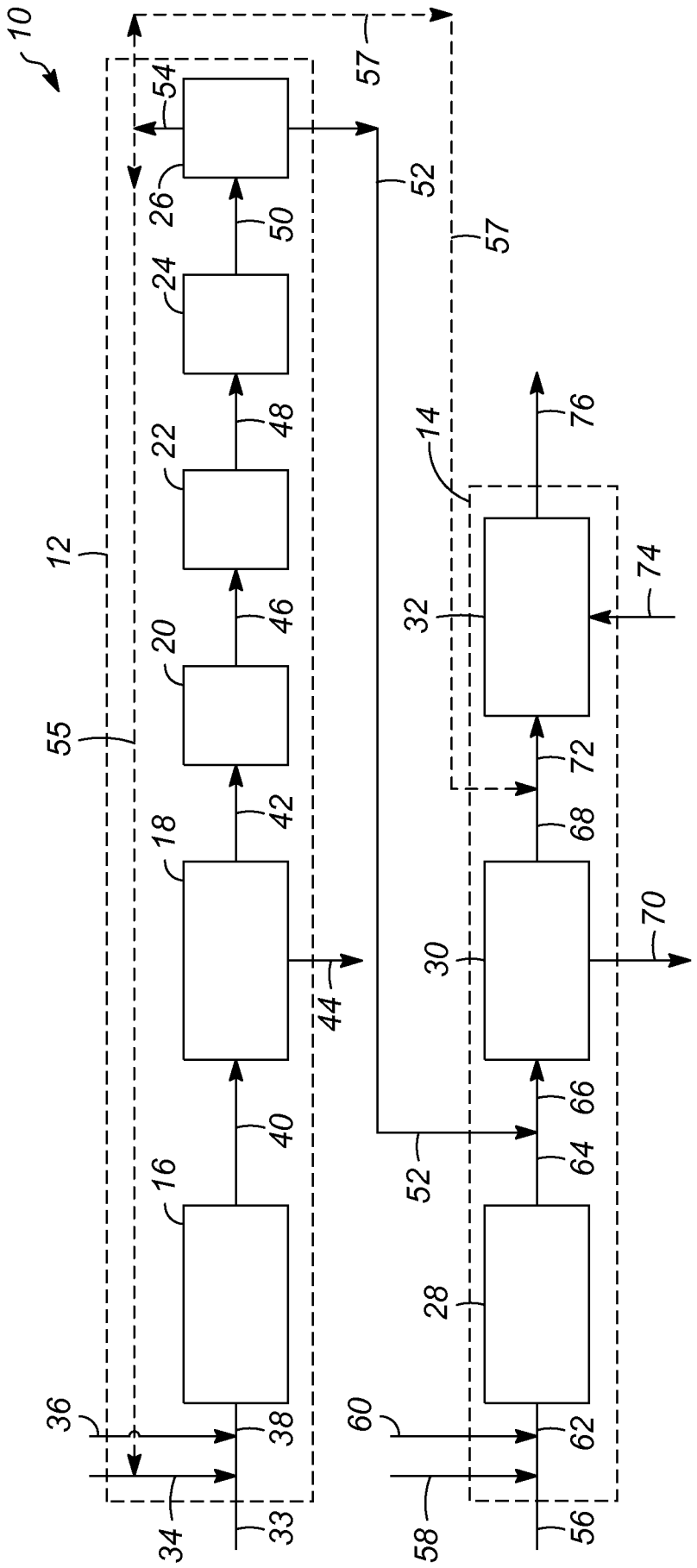

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FIG. 1

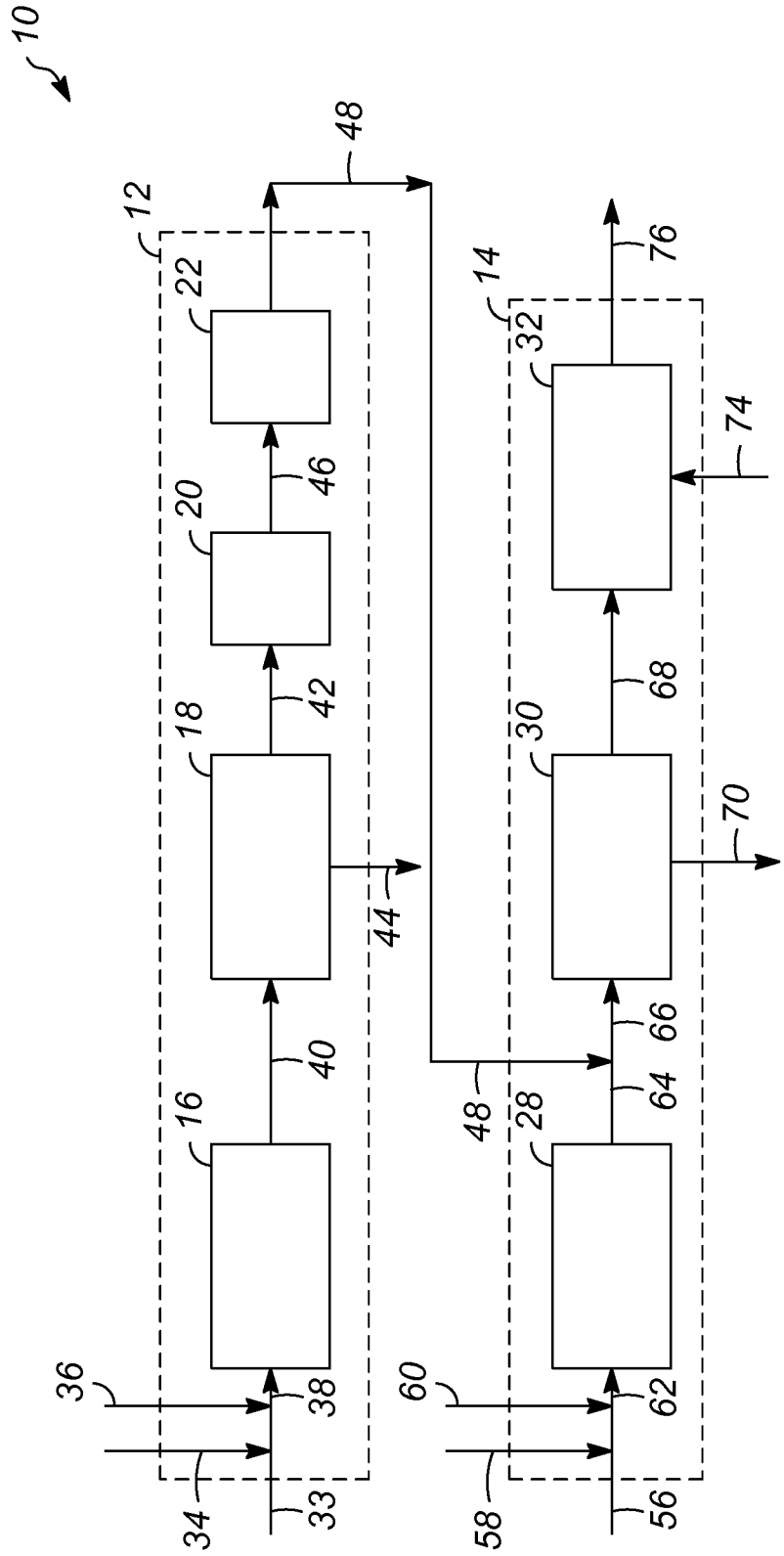

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FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2013/064566

A. CLASSIFICATION OF SUBJECT MATTER

C07C 9/08 *(2006.01)*
C07C 9/10 *(2006.01)*
C07C 5/27 *(2006.01)*

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)

C07C 9/08, 9/10, 5/27

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)

PAJ, Esp@cenet, USPTO DB, EAPATIS, Information Retrieval System of FIPS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0381881 A1 (UOP) 16.08.1990	1-10
A	US 4877919 A (UOP) 31.10.1989	1-10
A	JP 2142739 A (AGENCY OF IND SCIENCE & TECHNOL) 31.05.1990 (abstract)	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

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"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
25 December 2013 (25.12.2013)	30 January 2014 (30.01.2014)
Name and mailing address of the ISA/ FIPS Russia, 123995, Moscow, G-59, GSP-5, Berezhkovskaya nab., 30-1 Facsimile No. +7 (499) 243-33-37	Authorized officer A. Sedov Telephone No. (495)531-64-81

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