

METHODS AND APPARATUSES FOR ISOMERIZATION OF PARAFFINS

STATEMENT OF PRIORITY

[0001] This application claims priority to U.S. Application No. 13/434,703 which was
5 filed on March 29, 2012, the contents of which are hereby incorporated by reference in its
entirety.

TECHNICAL FIELD

[0002] The present invention relates generally to methods and apparatuses for
isomerization of hydrocarbons, and more particularly relates to methods and apparatuses
10 for isomerization of paraffins using a chloride-promoted isomerization catalyst.

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 that generally have higher octane ratings. Many isomerization processes
15 employ a chlorinated catalyst, such as chlorinated alumina catalyst, chlorinated platinum
aluminum catalyst, and the like, in a reaction zone. The chlorinated catalyst requires a
continuous addition of chloride to replace chloride removed from the surface of the
catalyst and carried away in the reaction-zone effluent. Typically, a fresh feed of chloride
promoter, such as perchloroethylene, is continuously introduced into a paraffin feed
20 stream upstream from a reactor in the reaction zone. Inside the reactor, the chloride
promoter decomposes to form hydrogen chloride that activates, e.g., promotes or
regenerates, the catalyst by replenishing the chloride removed from the catalyst's surface.

[0004] The reaction-zone effluent generally contains a significant amount of hydrogen
chloride from the continuous decomposition of chloride promoter and the removal of
25 chloride from the surface of the catalyst. A product stream containing branched paraffins
is separated from the reaction-zone effluent by removing hydrogen chloride and other
volatile light hydrocarbons (e.g., hydrocarbons having six or fewer carbons) as a stabilizer
vapor stream. Because hydrogen chloride poses environmental and handling concerns, the
stabilizer vapor stream is continuously scrubbed with a caustic, such as sodium hydroxide,
30 to neutralize the hydrogen chloride before removing the off-gas stream from the process.
The cost of chloride promoters and caustics are relatively expensive, and many refiners

would like to reduce their consumption of these components to improve their process efficiencies and reduce overall operational costs.

[0005] Accordingly, it is desirable to provide methods and apparatuses for isomerization of paraffins with reduced chloride promoter consumption and/or reduced caustic

5 consumption to improve process efficiencies and reduce overall operational costs.

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

10 [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 separating an isomerization effluent into a product stream that comprises branched and un-branched paraffins and a stabilizer vapor stream that comprises HCl, H₂, and C₆- hydrocarbons. A net gas vapor that comprises HCl, H₂, and

15 C₅- hydrocarbons is formed using the stabilizer vapor stream. The net gas vapor is separated into a C₅- hydrocarbons-rich phase and a HCl and H₂-rich stream. Forming the net gas vapor comprises separating the stabilizer vapor stream and the C₅- hydrocarbons-rich phase into the net gas vapor and a liquid stream that comprises C₂- and C₃⁺ hydrocarbon. An isomerization catalyst is activated using at least a portion of the HCl and

20 H₂-rich stream to form a chloride-promoted isomerization catalyst. A paraffin feed stream is contacted with the chloride-promoted isomerization catalyst in the presence of hydrogen for isomerization of the paraffins.

[0007] In accordance with another exemplary embodiment, a method for isomerization of paraffins is provided. The method comprises the steps of activating an isomerization

25 catalyst in a reactor operating at isomerization conditions to form a chloride-promoted isomerization catalyst. The isomerization catalyst is activated with HCl generated from a chloride promoter stream and from a HCl and H₂-rich recycle stream. A paraffin feed stream comprising un-branched paraffins is contacted with the chloride-promoted isomerization catalyst in the reactor in the presence of hydrogen to form an isomerization

30 effluent that comprises branched paraffins, HCl, H₂, and other C₇- hydrocarbons. The isomerization effluent is introduced to a stabilizer at stabilization conditions to form a product stream that comprises branched and un-branched paraffins and a stabilizer vapor

stream that comprises HCl, H₂, and C₆- hydrocarbons. A net gas vapor that comprises HCl, H₂, and C₅- hydrocarbons is formed in a separator at first separation conditions using the stabilizer vapor stream. The net gas vapor is separated in a chiller at second separation conditions into a C₅- hydrocarbons-rich phase and a HCl and H₂-rich stream. Forming the net gas vapor comprises separating the stabilizer vapor stream and the C₅- hydrocarbons-rich phase in the separator at the first separation conditions into the net gas vapor and a liquid stream that comprises C₂- and C₃⁺ hydrocarbons. At least a portion of the HCl and H₂-rich stream is recycled back to the reactor as the HCl and H₂-rich recycle stream.

[0008] In accordance with another exemplary embodiment, an apparatus for

isomerization of paraffins is provided. The apparatus comprises a stabilizer that is configured to receive an isomerization effluent and to operate at stabilization conditions effective to separate the isomerization effluent into a product stream that comprises branched and un-branched paraffins and a stabilizer vapor stream that comprises HCl, H₂, and C₆- hydrocarbons. A separator is configured to receive the stabilizer vapor stream and to operate at first separation conditions effective to form a net gas vapor that comprises HCl, H₂, and C₅- hydrocarbons using the stabilizer vapor stream. A chiller is configured to receive the net gas vapor and to operate at second separation conditions effective to separate the net gas vapor into a C₅- hydrocarbons-rich phase and a HCl and H₂-rich stream. The separator is further configured to receive the C₅- hydrocarbons-rich phase and to separate the stabilizer vapor stream and the C₅- hydrocarbons-rich phase at the first separation conditions into the net gas vapor and a liquid stream that comprises C₂- and C₃⁺ hydrocarbons. A reaction zone contains an isomerization catalyst. The reaction zone is configured to receive at least a portion of the HCl and H₂-rich stream and a paraffin feed stream and to operate at isomerization conditions to activate the isomerization catalyst to form a chloride-promoted isomerization catalyst for contact with the paraffin feed stream in the presence of hydrogen for isomerization of the paraffins. A LPG stripper is configured to receive at least a portion of the liquid stream and to operate at third separation conditions effective to separate the at least the portion of the liquid stream into a C₂- hydrocarbon-rich stream and a LPG stream that comprises C₃ and C₄ hydrocarbons.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The present invention 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.

DETAILED DESCRIPTION

[0011] The following Detailed Description is merely exemplary in nature and is not
5 intended to limit the invention or the application and uses of the invention. Furthermore, there is no intention to be bound by any theory presented in the preceding background or the following detailed description.

[0012] Various embodiments contemplated herein relate to methods and apparatuses for isomerization of paraffins. Unlike the prior art, the exemplary embodiments taught herein
10 introduce an isomerization reaction-zone effluent from an isomerization reaction zone to a stabilizer. 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 (e.g., reaction zone), heaters, exchangers, pipes, pumps, compressors, and controllers. Additionally, an equipment item, such as a reactor, dryer, or
15 vessel, can further include one or more zones or sub-zones. The isomerization reaction-zone effluent comprises HCl, H₂, branched and un-branched paraffins, and other C₇-hydrocarbons. As used herein, C_x means hydrocarbon molecules that have “X” number of carbon atoms, C_x⁺ means hydrocarbon molecules that have “X” and/or more than “X” number of carbon atoms, and C_x⁻ means hydrocarbon molecules that have “X” and/or less
20 than “X” number of carbon atoms. The stabilizer is operating at stabilization conditions effective to separate the isomerization reaction-zone effluent into a product stream that comprises the branched and un-branched paraffins and a stabilizer vapor stream that comprises HCl, H₂, and C₆-hydrocarbons.

[0013] Next, a portion of the C₆-hydrocarbons are removed from at least a portion of
25 the stabilizer vapor stream to form a HCl and H₂-rich stream. In an exemplary embodiment, C₆-hydrocarbons are removed from at least a portion of the stabilizer vapor stream using a separator and a chiller that are in fluid communication with each other. The stabilizer vapor stream is introduced to the separator. The separator is operating at separation conditions effective to form a net gas vapor that comprises HCl, H₂, and C₅-
30 hydrocarbons. In an exemplary embodiment, the net gas vapor is introduced to the chiller. The net gas vapor is separated in the chiller at separation conditions effective to form a C₅-hydrocarbons-rich phase and the HCl and H₂-rich stream. In an exemplary embodiment,

the chiller is mounted directly on the separator such that the C₅- hydrocarbons-rich phase returns back to the separator. The separator forms the net gas vapor and a liquid stream that comprises C₂- and C₃⁺ hydrocarbons by separating the stabilizer vapor stream and the C₅- hydrocarbons-rich phase at the separation conditions. In an exemplary embodiment, a portion of the liquid stream is directed to a LPG stripper. The LPG stripper is operating at conditions effective to separate the portion of the liquid stream into a C₂- hydrocarbon-rich stream and a LPG stream that comprises C₃ and C₄ hydrocarbons. The HCl and H₂-rich stream is divided into a recycle portion and a treatment portion. The treatment portion of HCl and H₂-rich stream is directed to a scrubber for treatment with a caustic. Because only a portion of HCl and H₂-rich stream is being directed to the scrubber, less HCl is being treated than conventional processes and thus, less caustic is required for neutralizing the HCl. Therefore, caustic consumption can be reduced for the isomerization process.

[0014] In an exemplary embodiment, the recycle portion of the HCl and H₂-rich stream is introduced to a reactor in the isomerization reaction zone. The reactor contains an isomerization catalyst and is operating at isomerization conditions. The isomerization catalyst is contacted with the recycle portion of the HCl and H₂-rich stream to activate the isomerization catalyst by replenishing chloride removed from the surface of the isomerization catalyst, forming a chloride-promoted isomerization catalyst. Because the recycle portion of the HCl and H₂-rich stream is used to activate the isomerization catalyst, less chloride promoter is required for activating the isomerization catalyst. Therefore, chloride promoter consumption can be reduced for the isomerization process. Also, since H₂ is also contained in the recycle portion of the HCl and H₂-rich stream, less makeup hydrogen is required and hydrogen consumption is reduced. A feed stream containing paraffins is introduced to the reactor and contacts the chloride-promoted isomerization catalyst in the presence of hydrogen to isomerize the paraffins and form branched paraffins.

[0015] Referring to FIG. 1, a schematic depiction of an apparatus 10 for isomerization of paraffins is provided. The apparatus 10 is utilized for a paraffin isomerization process that converts normal paraffins to branched paraffins. The apparatus 10 comprises a reaction zone 12 and a stabilizing-scrubbing zone 14.

[0016] The reaction zone 12 and the stabilizing-scrubbing zone 14 include a reactor 18 and stabilizer 20 (e.g., distillation column), respectively, that are in fluid communication.

A paraffin feed stream 22 containing normal or un-branched paraffins is passed through a dryer 24 for removing water and to form a dried paraffin feed stream 26. In one embodiment, the paraffin feed stream 22 is rich in C₄ hydrocarbons, such as n-butane and may also contain relatively small amounts of iso-butane, pentane, and heavier materials (e.g., C₆⁺ hydrocarbons). In another embodiment, the paraffin feed stream 22 is rich in C₅ and/or C₆ hydrocarbons, such as normal pentane and normal hexane.

[0017] In an exemplary embodiment, a hydrogen-containing gas feed 28 is passed through a dryer 30 for removing water and is combined with the dried paraffin feed stream 26 to form a combined stream 32. The combined stream 32 is passed through a heat exchanger 34 and a heater 36. As illustrated and will be discussed in further detail below, a chloride promoter stream 38 (e.g., containing perchloroethylene or the like) is introduced to the combined stream 32 between the heat exchanger 34 and the heater 36, and a HCl and H₂-rich recycle stream 40 (e.g., containing 0.1 weight percent (wt. %) or greater of HCl) is introduced to the combined stream 32 upstream from the heat exchanger 34. In an exemplary embodiment, the heat exchanger 34 and the heater 36 together heat the combined stream 32 to a temperature of from 90 to 210°C for introduction to the reactor 18.

[0018] In an exemplary embodiment, the reactor 18 is 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 from the HCl and H₂-rich recycle stream 40 and further, by the decomposition of chloride promoter from the chloride promoter stream 38 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., iso-butane, branched pentane, branched hexane, or combinations thereof) to produce an isomerization reaction-zone effluent 42. The isomerization reaction-zone effluent 42 contains the branched and un-branched paraffins, other C₇- hydrocarbons, H₂, HCl, and possibly other chloride-containing compounds. The isomerization reaction-zone effluent 42 is passed through the heat exchanger 34 to cool the effluent 42 to a temperature of from 65 to 165°C.

[0019] The isomerization reaction-zone effluent 42 is then introduced to the stabilizer 20. The stabilizer 20 separates the isomerization reaction-zone effluent 42 into a product stream 44 and a stabilizer vapor stream 46. The stabilizer vapor stream 46 contains HCl, H₂, and C₆- hydrocarbons. The product stream 44 contains branched and un-branched paraffins and is removed from the stabilizing-scrubbing zone 14. A portion of the product stream 44 may be passed through a heater 45 and returned back to the stabilizer 20 as reflux.

[0020] In an exemplary embodiment, the stabilizer vapor stream 46 is passed through an air cooler 48 and a partial condenser 50 that together cool the stabilizer vapor stream 46 to a temperature of from 30 to 60°C. The stabilizer vapor stream 46 is then introduced to a separator 52 for separation together with a C₅- hydrocarbon-rich phase (e.g. from a chiller 82) as will be discussed in further detail below. A liquid stream 54 containing C₂- and C₃⁺ hydrocarbons is removed from the separator 52 and is passed through a pump 56. A level controller 58 including a control valve 60 controls the flow of the liquid stream 54 being removed from the separator 52.

[0021] In an exemplary embodiment, the stabilizing-scrubbing zone 14 comprises an LPG stripper 74. As illustrated, the liquid stream 54 is divided into portions 75 and 76. The portion 75 of the liquid stream 54 is advanced to the stabilizer 20 for reflux. The portion 76 of the liquid stream 54 is introduced to the LPG stripper 74. A level controller 77 and control valve 78 control the amount of the portion 76 flowing into the LPG stripper 74. The LPG stripper 74 is operating at separation conditions effective to separate the portion 76 of the liquid stream 54 into a C₂- hydrocarbon-rich stream 80 and a LPG stream 81 that comprises C₃ and C₄ hydrocarbons. In an exemplary embodiment, the separation conditions of the LPG stripper 74 include a temperature of from 65 to 120°C and a pressure of from 1,000 to 2,000 kPa. As illustrated, the C₂- hydrocarbon-rich stream 80 is combined with the stabilizer vapor stream 46 upstream from the air cooler 48 and the partial condenser 50 for introduction to the separator 52. The LPG stream 81 is removed from the stabilizing-scrubber zone 14 for storage or otherwise. As illustrated, a portion of the LPG stream 81 may be passed through a heater 70 and returned back to the LPG stripper 74 as reflux.

[0022] Volatiles including HCl, H₂, and C₅- hydrocarbons form a net gas vapor in the separator 52. In an exemplary embodiment, the separator 52 is operating at a pressure of

from 700 to 2,100 kPa. In an exemplary embodiment, the net gas vapor enters a chiller 82 that is mounted directly on the separator 52. Alternatively, the chiller 82 may be positioned downstream from the separator 52. In an exemplary embodiment, the net gas vapor is cooled in the chiller 82 via indirect heat exchange with a refrigerant 83, e.g., propane or the like, to a temperature of from -40 to 5°C. In an exemplary embodiment, the net gas vapor in the chiller 82 is at a pressure of from 700 to 2,100 kPa. The net gas vapor is separated into a HCl and H₂-rich stream 62 and a C₅- hydrocarbons-rich phase. In an exemplary embodiment, the C₅- hydrocarbons-rich phase drops back into the separator 52 for separation with the stabilizer vapor stream 46 as discussed above. In an exemplary embodiment, the HCl and H₂-rich stream 62 comprises HCl present in an amount of 0.1 wt. % or greater, such as from 0.2 to 0.7 wt. %, and H₂.

[0023] As illustrated, a pressure controller 64 along with control valves 66 and 68 are used to divide the HCl and H₂-rich stream 62 into a recycle portion, i.e., the HCl and H₂-rich recycle stream 40, and a treatment portion 72, respectively. The HCl and H₂-rich recycle stream 40 is passed through a compressor 86. In an exemplary embodiment, the compressor 86 pressurizes the HCl and H₂-rich recycle stream 40 to a pressure of from 1,700 to 3,500 kPa. The HCl and H₂-rich recycle stream 40 is passed along from the compressor 86 and is combined with the combined stream 32 for introduction to the reactor 18 together with the chloride promoter stream 38. As discussed above, once introduced to the reactor 18, HCl from the from the HCl and H₂-rich recycle stream 40 and further from the decomposition of chloride promoter from the chloride promoter stream 38 contacts and activates the isomerization catalyst by replenishing chloride removed from the surface of the isomerization catalyst. Because the HCl and H₂-rich recycle stream 40 is used to activate the isomerization catalyst, less chloride promoter is required from the chloride promoter stream 38 for activating the isomerization catalyst.

[0024] The treatment portion 72 of the HCl and H₂-rich stream 62 is passed through a heat exchanger 98 for indirect heat exchange with a heat transfer fluid 100, such as steam. In an exemplary embodiment, the heat exchanger 98 heats the treatment portion 72 of the HCl and H₂-rich stream 62 to a temperature of from 30 to 70°C. The treatment portion 72 of the HCl and H₂-rich stream 62 is then passed to a scrubber 104. The scrubber 104 scrubs the treatment portion 72 of the HCl and H₂-rich stream 62 by neutralizing any HCl

contained therein with a caustic 106 followed by counter flow contact with water 108 to form a neutralized stream 110 and a caustic waste stream 112.

[0025] Accordingly, methods and apparatuses for isomerization of paraffins have been described. The exemplary embodiments taught herein introduce an isomerization

5 reaction-zone effluent from an isomerization reaction zone to a stabilizer. The isomerization reaction-zone effluent comprises HCl, H₂, branched and un-branched paraffins, and other C₇- hydrocarbons. The stabilizer separates the isomerization reaction-zone effluent into a product stream that comprises the branched and un-branched paraffins and a stabilizer vapor stream that comprises HCl, H₂, and C₆- hydrocarbons. A portion of
10 C₆- hydrocarbons are removed from the stabilizer vapor stream using a separator and a chiller that are in fluid communication with each other. The separator and the chiller cooperate to separate the stabilizer vapor stream to form a HCl and H₂-rich stream. A treatment portion of the HCl and H₂-rich stream is directed to a scrubber for treatment with a caustic. Because only a portion of the HCl and H₂-rich stream is being directed to
15 the scrubber, less HCl is being treated than conventional processes and thus, less caustic is required for neutralizing the HCl. A recycle portion of the HCl and H₂-rich stream is introduced to a reactor in the isomerization reaction zone. The reactor contains an isomerization catalyst that is contacted with the HCl and H₂-rich stream to form a chloride-promoted isomerization catalyst. Because the recycle portion of the HCl and H₂-
20 rich stream is used to activate the isomerization catalyst, less chloride promoter is required for activating the isomerization catalyst.

[0026] 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

25 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
30 exemplary embodiment without departing from the scope of the disclosure as set forth in the appended claims.

CLAIMS

What is claimed is:

- 5 1. A process for hydrocarbon distillation comprising:
 providing a hydrocarbon feed stream (130) to a fractionation zone (125) at
a first position;
 fractionating the hydrocarbon feed stream (130) into an overhead stream
(140) and a bottoms stream (145);
10 heating (200) a first portion of the overhead stream (190) to a temperature
above a dew point temperature of the overhead stream (140);
 compressing (205) the heated first overhead stream portion (190);
 removing a portion of a stream (215) from the fractionation zone (135) at a
second position below the first position;
15 heating (220) the removed stream portion (215) by indirectly contacting the
removed stream portion (215) with the compressed first overhead stream portion (210);
 returning the heated removed stream portion (215) to the fractionation zone
(135) at a third position above the second position and below the first position;
 reducing the pressure (235) of the compressed first overhead stream portion
20 to form a reduced pressure overhead stream (240);
 returning a portion (180) of the reduced pressure overhead stream to the top
of the fractionation zone (135);
 wherein heating (200) the first overhead stream portion (190) comprises
indirectly contacting the first overhead stream portion (190) with the compressed first
25 overhead stream portion (225) after indirectly contacting the removed stream portion (215)
with the compressed first overhead stream portion (210).
2. The process of claim 1 further comprising removing a side cut (160) from the
fractionation zone (135) at a fourth position below the first position, the side cut (135)
having a boiling point between a boiling point of the overhead stream (140) and a boiling
point of the bottoms stream (145).

3. The process of any of claims 1-2 further comprising combining the reduced pressure overhead stream (240) with a second overhead stream portion (195).
4. The process of any of claims 1-3 wherein indirectly contacting the removed stream portion (215) with the compressed first overhead stream portion (210) comprises heating the removed stream portion (215) in a heat exchanger.
5. The process of any of claims 1-4 wherein a temperature difference between the overhead stream (140) and the bottoms stream (145) is at least 38.9°C (70°F).
6. The process of any of claims 1-5 wherein the hydrocarbon feed stream (130) contains primarily C₅-C₆ hydrocarbons, wherein the overhead stream (140) contains primarily di-methyl butane and lighter hydrocarbons, and wherein the bottoms stream (145) contains primarily C₇₊ hydrocarbons.
- 5 7. The process of claim 6 further comprising removing a side cut (160) from the fractionation zone (135) at a fourth position below the first position and above the third position, the side cut (160) having a boiling point between a boiling point of the overhead stream (140) and a boiling point of the bottoms stream (145), and wherein the side cut (160) contains primarily methyl pentanes, normal hexane, and C₆ naphthenes.
8. The process of any of claims 1-5 wherein the hydrocarbon feed stream (130) contains primarily C₅-C₆ hydrocarbons with little to no C₇₊ hydrocarbons, wherein the overhead stream (140) contains primarily di-methyl butane and lighter hydrocarbons, and
10 wherein the bottoms stream (145) contains primarily methyl pentanes, normal hexane, and C₆ naphthenes.
9. The process of claim 1 wherein the hydrocarbon feed stream (130) contains primarily C₄ hydrocarbons, wherein the overhead stream (140) contains primarily isobutane and lighter hydrocarbons, and wherein the bottoms stream (145) contains primarily C₅₊ hydrocarbons.

10. A distillation column and heat pump comprising:

the distillation column (135) having a feed inlet at a first position, an overhead outlet, and a bottoms outlet;

5 a reboiler (220) having an inlet and an outlet, the reboiler inlet in fluid communication with a second position below the first position, and the reboiler outlet being in fluid communication with a third position on the distillation column, the third position being above the second position and below the first position;

a heat exchanger (200) in heat exchange communication with at least a portion of the distillation column overhead outlet;

10 a compressor (205) having a compressor inlet in fluid communication with at least the portion of the distillation column overhead outlet and a compressor outlet in heat exchange communication with the reboiler and the heat exchanger; and

15 an expansion valve (235) having an expansion valve inlet in fluid communication with the compressor outlet and an expansion valve outlet in fluid communication with an inlet at a position above the first position and below the overhead outlet.