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(54) Title: PROCESS FOR PRODUCING AROMATICS FROM METHANE WITH INTERMEDIATE COX COFEEDING

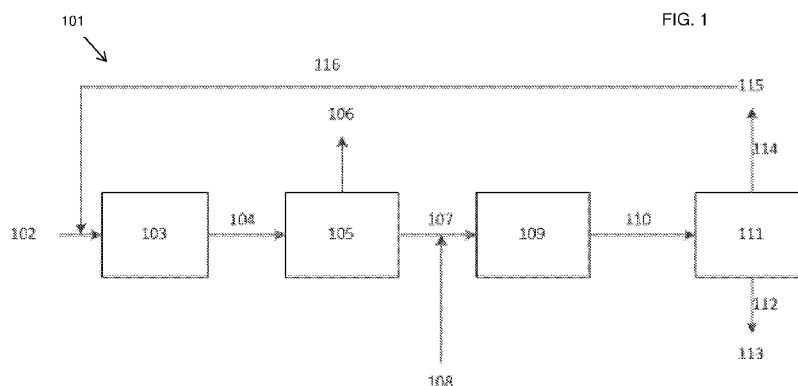


FIG. 1

(57) Abstract: Systems and methods for integrated production of aromatics are described. Systems and methods can include a process for producing aromatics, such as benzene, toluene, naphthalene, or other aromatics by providing methane to a first reactor to produce a first product stream comprising aromatics, such as benzene, toluene, naphthalene, or other aromatics and hydrogen; recovering the aromatics from the first product stream and mixing the first product stream with a carbon dioxide and/or steam feed stream; providing the combined aromatics depleted first product stream and carbon dioxide feed stream to a second reactor to produce a second product stream containing water and synthetic or unconverted methane; and adding the recycled methane to new methane-containing feedstock for future integrated production of aromatics.

PROCESS FOR PRODUCING AROMATICS FROM METHANE
WITH INTERMEDIATE CO_x COFEEDING

TECHNICAL FIELD

[0001] The present invention relates to systems and methods for producing aromatics and other chemicals, and more specifically, to a process for producing aromatics and other chemicals from methane-containing feedstocks.

BACKGROUND

[0002] Benzene has many uses in chemical industries, and demand for benzene continues to grow significantly each year.

[0003] Benzene has traditionally been obtained from a petroleum feed source. Industrial benzene production generally uses one of the following chemical processes: catalytic reforming, toluene hydrodealkylation, toluene disproportionation, and steam cracking. Traditional processes for creating benzene are becoming less economically viable as petroleum feed sources are becoming more expensive. Natural gas is poised to replace petroleum as one of the primary source materials used by the petrochemical industry. Direct conversion of methane (CH₄) to aromatics produces benzene at very high selectivity, with hydrogen as the main by-product. The separation of hydrogen from the benzene product, however, requires an expensive separation process, typically cryogenic separation, pressure swing adsorption (PSA), or both.

[0004] Due to the thermodynamic limitations of methane dehydroaromization, the unconverted methane exists as the dominant component in the product stream of the methane dehydroaromization reactor. It is preferable to remove the by-product hydrogen from the recycled stream because as concentrations increase, it creates unfavorable reaction thermodynamics to methane dehydroaromization. Separation of hydrogen from the product stream, however, is difficult requiring an expensive separation process, typically cryogenic separation, PSA, or both. U.S. No. Patent 8,138,384 (incorporated by reference in its entirety) fails to describe the use of a carbon dioxide stream.

[0005] Needs exist for a process that does not require hydrogen separation without compromising the thermodynamics for methane dehydroaromization. Needs also exist for recycling the unconverted methane to improve the overall process economics for methane dehydroaromization.

SUMMARY

[0006] Embodiments of the present invention solve many of the problems and/or overcome many of the drawbacks and disadvantages of the prior art by providing systems and methods for producing aromatics and recycling unconverted methane in an integrated process.

[0007] Embodiments of the present invention may include systems and methods for producing aromatics and other chemicals in an integrated process. The systems and methods can include a process for producing aromatics and other chemicals. The method can include providing methane feedstock to a first reactor to produce a first product stream comprising aromatics and hydrogen, wherein the methane feedstock is contacted with a catalyst; recovering aromatics from the first product stream to create an aromatics depleted resulting stream; mixing the aromatics depleted resulting stream with a feed stream to create a combined product stream; and providing the combined product stream to a second reactor to produce a second product stream comprising water and unconverted methane.

[0008] Embodiments of the present invention can include systems and methods for producing aromatics and other chemicals from recycled methane feedstock. The method can include receiving recycled methane from a methanation reaction; mixing the recycled methane and methane feedstock to form a combined methane feedstock; providing the combined methane feedstock to a first reactor to produce a first product stream comprising aromatics and hydrogen, wherein the combined methane feedstock is contacted with a catalyst; recovering aromatics from the first product stream to create an aromatics depleted resulting stream; mixing the aromatics depleted resulting stream with a feed stream to create a combined product stream; and providing the combined product stream to a second reactor to produce a second product stream comprising synthetic methane or unconverted methane, and water.

[0009] Embodiments of the present invention can include systems and methods for producing a methane-rich gas. The method can include receiving a first resulting stream from one or more dehydroaromatization reactions; extracting aromatics from the first resulting stream, wherein the resulting stream is converted to an aromatic depleted resulting stream; mixing the aromatics depleted resulting stream with a carbon dioxide feed or steam feed stream to create a combined stream; mixing the combined stream with one or more methanation catalysts in a methanation reactor to produce a second resulting stream; and extracting water from the second resulting stream.

[0010] Additional features, advantages, and embodiments of the invention are set forth or apparent from consideration of the following detailed description, drawings and claims. Moreover, it is to be understood that both the foregoing summary of the invention and the following detailed description are exemplary and intended to provide further explanation without limiting the scope of the invention as claimed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] The accompanying drawings, which are included to provide a further understanding of the invention and are incorporated in and constitute a part of this specification, illustrate preferred embodiments of the invention and together with the detailed description serve to explain the principles of the invention. In the drawings:

[0012] FIGS. 1 and 2 show exemplary integrated systems for producing aromatics from a methane-containing feed stock and recycling synthetic methane or unconverted methane for use in future aromatic production.

DETAILED DESCRIPTION

[0013] Systems and methods are described for the integrated processes 101 for the conversion of feedstocks, such as methane and carbon dioxide, to benzene, methanol, olefins, oxo products, Fischer–Tropsch (FT) products, and other aromatics. The processes described herein are exemplary processes only and used for illustrative purposes. Other variations and combinations of steps and components can be used as necessary.

[0014] In certain embodiments of the present invention, an integrated process 101 can be divided into several different components. FIG. 1 is a flow diagram illustrating an exemplary integration process of the current invention.

[0015] In a first component of an exemplary integrated process 101, methane-containing feedstock from feed line 102 can be converted to aromatics and hydrogen via a dehydroaromatization reaction, and/or other hydrocarbons via dehydrogenation-coupling reactions in reactor 103. In some alternatives, conversion of the methane-containing feedstock can involve contacting the methane-containing feedstock with one or more catalysts at the dehydromatization reactor 103. In some alternatives, the one or more catalysts can include a bifunctional Zeolite supported metal catalyst. In some alternatives, the metal function can include but is not limited to any of the following individually or in a combination: molybdenum, tungsten, ruthenium, iron, cobalt, nickel, copper, silver, zinc, chromium, or tin. In some alternatives, the zeolite function can include but is not limited to

pentasil type zeolite family, modified pentasil type zeolites family, or other medium pore zeolites such as zeolite beta and zeolite MCM-22. In some alternatives, the integrated process 101 can include one or more simultaneous dehydrogenation and cyclization (dehydrocyclization) steps. The dehydrocyclization steps can be conducted over a wide range of conditions, such as temperature, pressure or gaseous hourly space velocity (GHSV) of the feed gas. Typically, the dehydrocyclization steps can be conducted at a temperature of about 400°C to about 1000°C, about 500°C to about 850°C, or about 700°C to about 750°C. Typically, the dehydrocyclization steps can be conducted at an absolute pressure of 0.2 – 5 atmosphere (0.02 to 0.5 MegaPascals (MPa)), and more preferably 0.5 - 2 atmosphere (0.05 to 0.2 MPa). Typically, the dehydrocyclization steps can be conducted at a GHSV of the feed gas in terms of volumes of gas per volume of catalyst per hour can be about 400 to about 8,000 GHSV or about 500 to about 7,000 GHSV.

[0016] The product stream coming from the reactor 103 via line 104 can be fed to a condenser or separator 105. In some alternatives, the condenser or separator 105 can be a cryogenic separator where the aromatics can be recovered from the condenser or separator 105 via line 106. In some alternatives, the aromatics can include benzene, toluene, naphthalene, and/or other aromatics. The aromatic depleted reaction product of the dehydroaromatization reaction can then be sent via transfer line 107. A feed containing carbon dioxide and steam (water) can be added via line 108 and can be mixed with the aromatic depleted reaction product of the dehydroaromatization reaction in transfer line 107. The volume ratio of steam to carbon dioxide can be increased from 0 up to 1. This combined feed of carbon dioxide, steam and the aromatic depleted reaction product in transfer line 107 can be fed to a Methanation reactor 109 to produce a product stream. In another component of the exemplary integrated process 101, the combined feed in methanation reactor 109 can be contacted with one or more methanation catalysts to produce a product stream. In some alternatives, the product stream can contain high concentration of unconverted methane 115.

[0017] In some alternatives, such as shown in FIG. 2, unconverted methane can be separated from aromatic depleted stream from line 107 using separator 201 and can be mixed with line 116 via line 202. The resulting stream from separator 201 can then be sent via transfer line 203. A feed containing carbon dioxide and steam (water) can be added via line 108 and can be mixed with the resulting stream in transfer line 203 to create a combined stream. The combined stream can then be mixed with one or more methanation catalysts in a methanation reactor 109 to produce a second resulting stream consisting of synthetic methane. Water 113 can be extracted from the synthetic methane stream via line 112.

[0018] In some alternatives, methanation catalysts can include ruthenium, cobalt, nickel or iron. The product stream coming from reactor 109 via line 110 can be fed to a separator 111. Water 113 can be recovered from the separator 111 via line 112. In some alternatives, the recovered water 113 can be used for other reactions. Recycled methane 115 can be recovered from the separator 111 via line 114. Recycled methane 115 can be sent via line 116 to be combined in line 102 with methane-containing feedstock from feed line 102 for producing aromatics and other chemicals in the future using the exemplary integrated process 101. In some alternatives, the methanation reactions can be conducted over a range of conditions, such as temperature, pressure and GHSV of combined feed gas. Typically, the methanation reactions temperature can be about 200°C to about 600° C, and more preferably about 300°C to about 575°C, and most preferably about 550°C. Typically, the methanation reactions pressure can be about 0 to about 10,000 pound per square inch (psi) (about 0 MPa to about 70 MPa). Typically, the methanation reactions GHSV of combined feed gas in terms of volumes of gas per volume of catalyst per hour can be about 200 to about 10,000 GHSV or about 600 to about 5,000 GHSV.

[0019] Elimination of the need to separate the hydrogen by-product from the output stream of the dehydroaromatization reaction adds significant value to the exemplary integrated process by reducing time, cost and energy requirements. The integrated process 101 brings considerable savings by avoiding costly hydrogen separation steps and improving energy/site efficiency by producing other valuable downstream products, such as methanol, Dimethyl Ether (DME) and other aromatics.

[0020] A feed stock of methane can be introduced via feed line 102 into a first reactor 103. Any methane-containing feedstock can be used in the present process but, in general, the present process can be used with a natural gas feedstock. Other suitable methane-containing feedstocks can include those obtained from sources such as coal beds, landfills, agricultural or municipal waste fermentation, or refinery gas streams. Methane-containing feedstocks, such as natural gas, typically contain carbon dioxide and ethane in addition to methane. Ethane and other aliphatic hydrocarbons that can be present in the feedstock can, of course, be converted to desired aromatic products in a dehydroaromatization step. Nitrogen and sulfur impurities are also typically present in methane-containing streams and can be removed or reduced to acceptable levels prior to use of the streams as disclosed herein. In certain embodiments, the feed to the dehydroaromatization step can contain less than approximately 100 parts per million (ppm), less than approximately 10 ppm, or less than approximately 1 ppm each of nitrogen and sulfur compounds.

[0021] Generally, the feedstock lower molecular weight hydrocarbon of the present invention can include methane or natural gas containing C₁ to C₄ hydrocarbons. In certain embodiments, the feed to the dehydroaromatization step in 103 can include approximately 95 to approximately 99.9 mol %, more preferably 97 to approximately 99 mol % methane.

[0022] The first reactor 103 can convert the methane-containing feedstock to benzene and hydrogen via a dehydroaromatization reaction. The dehydroaromatization step can be conducted in one or more fixed beds, moving beds, or fluidized bed reactors, with catalyst regeneration being conducted in-situ or ex-situ with air, oxygen, carbon dioxide, carbon monoxide, water, H₂, or combinations thereof.

[0023] The dehydroaromatization reaction is endothermic and, hence when the reaction is conducted in a plurality of stages, it can be necessary to employ inter-stage heating to return the feed to the required reaction temperature. The fuel required to provide the inter-stage heating can be obtained by removing and combusting a side stream from the dehydroaromatization effluent, after separation of the aromatic components and/or alkylated aromatic components. In addition, when the reaction occurs in the presence of a moving bed of catalyst, a portion or all of the heat can be supplied by withdrawing a portion of the catalyst from the bed, heating the catalyst by, for example, combustion of coke on the catalyst and then returning the heated catalyst to the moving catalyst bed.

[0024] The major components of the effluent from the dehydroaromatization step are H₂, benzene, naphthalene, and unconverted methane. Small amounts of ethylene, propylene, toluene, and carbon monoxide can also exist in the effluent. Typically, the effluent can contain a concentration of aromatic rings which is at least 5 weight percent (wt %), or at least 10 wt %, or at least 15 wt %, or preferably at least 20 wt % greater than the concentration of aromatic rings in the feed.

[0025] The benzene and other aromatics can then be recovered from the dehydroaromatization effluent, for example, by solvent extraction followed by fractionation. After recovery of the aromatic hydrocarbons from the dehydroaromatization effluent, the hydrogen in the effluent can be reacted with CO₂, and/or H₂O, to produce a new effluent gas mixture, which can contain synthetic or unconverted methane 115, hydrogen, carbon monoxide, carbon dioxide, and water.

[0026] In some alternatives, synthetic or unconverted methane 115 can come from the methanation step above and can be recycled back to the dehydroaromatization reactor feed stream preheater together with the fresh methane coming from feed line 102. Most of the synthetic or unconverted methane 115 can be recycled under pressure to the feed line 116 of

the dehydroaromatization reactor 103 without a compressor, and thus with no energy loss. The synthetic or unconverted methane 115 can be recycled at a temperature of 300°C to 600°C, and a pressure of 300 to 3000 kiloPascals (kPa).

[0027] The following example is merely illustrative of the method disclosed herein and is not intended to limit the scope hereof.

Example 1

[0028] In this simulation example, approximately 1,000 moles/hour (moles/hr) of combined feed gas containing 400 moles/hr of pure methane and 600 moles/hr of recycled methane, respectively, is fed to the dehydroaromatization reactor 103 via feed line 102. The dehydroaromatization reaction is conducted at a temperature of 525°C and a pressure of 3000 kPa. At the aromatics separator 105, approximately 100 moles/hr of aromatics is recovered via line 106. Line 107 feeding the methanation reactor 109, which contains approximately 1300 moles/hr of aromatics depleted reaction product from separator 105. The aromatics depleted reaction product contains unreacted methane, hydrogen and ethylene, and approximately 225 moles/hr of carbon dioxide. Carbon dioxide is fed via line 108. The methanation reactor 109 is operated at a temperature of 425°C and a pressure of 2500 kPa. The conversion of carbon dioxide can be greater than ninety-nine percent. Line 110 exiting the methanation reactor 109 contains approximately 225 moles/hr steam (water), and 600 moles/hr of methane, comprising synthetic methane, unreacted methane, and other fuel gas components. In the separator 111, recycled methane 115 is recovered from the separator 111 via line 114 and recycled back to dehydroaromatization reactor 103 via feed line 116. The water (steam) 113 is removed via line 112. The recovered water 113 can be used for other reactions after appropriate purification to acceptable levels.

[0029] The process disclosed herein includes at least the following embodiments:

[0030] Embodiment 1: A process for producing aromatics and other chemicals, comprising: providing methane feedstock to a first reactor to produce a first product stream comprising aromatics and hydrogen, wherein the methane feedstock is contacted with a catalyst; recovering aromatics from the first product stream to create an aromatics depleted resulting stream; mixing the aromatics depleted resulting stream with a feed stream to create a combined product stream; and providing the combined product stream to a second reactor to produce a second product stream comprising water and unconverted methane.

[0031] Embodiment 2: The process of Embodiment 1, wherein the first reactor produces the first product stream by dehydroaromatization.

[0032] Embodiment 3: The process of Embodiment 1 or Embodiment 2, wherein the second reactor is a methanation reactor.

[0033] Embodiment 4: The process of any of Embodiments 1 to 3, wherein the aromatics are recovered from the first product stream prior to entering the second reactor.

[0034] Embodiment 5: The process of any of Embodiments 1 to 4, wherein the feed stream is selected from a carbon dioxide feed stream, a steam feed stream, and combinations thereof.

[0035] Embodiment 6: The process of any of Embodiments 1 to 5, wherein the aromatics are selected from benzene, toluene, naphthalene, other aromatics, and combinations thereof.

[0036] Embodiment 7: The process of any of Embodiments 1 to 6, wherein the catalyst is a bifunctional Zeolite supported metal catalyst.

[0037] Embodiment 8: The process of Embodiment 7, wherein the metal is selected from molybdenum, tungsten, ruthenium, iron, cobalt, nickel, copper, silver, zinc, chromium, or tin, and combinations thereof.

[0038] Embodiment 9: A process for producing aromatics and other chemicals from recycled methane feedstock, comprising: receiving recycled methane from a methanation reaction; mixing the recycled methane and methane feedstock to form a combined methane feedstock; providing the combined methane feedstock to a first reactor to produce a first product stream comprising aromatics and hydrogen, wherein the combined methane feedstock is contacted with a catalyst; recovering aromatics from the first product stream to create an aromatics depleted resulting stream; mixing the aromatics depleted resulting stream with a feed stream to create a combined product stream; and providing the combined product stream to a second reactor to produce a second product stream comprising synthetic or unconverted methane, and water.

[0039] Embodiment 10: The process of Embodiment 9, wherein the first reactor produces the first product stream by dehydroaromatization.

[0040] Embodiment 11: The process of Embodiment 9 or Embodiment 10, wherein the second reactor is a methanation reactor.

[0041] Embodiment 12: The process of any of Embodiments 9 to 11, wherein the carbon dioxide or steam feed stream is a carbon dioxide feed stream.

[0042] Embodiment 13: The process of any of Embodiments 9 to 12, wherein the feed stream is selected from a carbon dioxide feed stream, a steam feed stream, and combinations thereof.

[0043] Embodiment 14: The process of any of Embodiments 9 to 13, wherein the aromatics are selected from a group consisting of: benzene, toluene, naphthalene, other aromatics and combinations thereof.

[0044] Embodiment 15: The process of any of Embodiments 9 to 14, wherein the catalyst is a bifunctional Zeolite supported metal catalyst.

[0045] Embodiment 16: The process of any of Embodiments 9 to 15, wherein the metal is selected from molybdenum, tungsten, ruthenium, iron, cobalt, nickel, copper, silver, zinc, chromium, or tin, and combinations thereof.

[0046] Embodiment 17: A process for producing a methane-rich gas, comprising: receiving a first resulting stream from one or more dehydroaromatization reactions; extracting aromatics from the first resulting stream, wherein the resulting stream is converted to an aromatic depleted resulting stream; mixing the aromatics depleted resulting stream with a carbon dioxide feed or steam feed stream to create a combined stream; mixing the combined stream with one or more methanation catalysts in a methanation reactor to produce a second resulting stream; and extracting water from the second resulting stream.

[0047] Embodiment 18: The process of Embodiment 17, wherein the aromatics are selected from benzene, toluene, naphthalene, other aromatics, and combinations thereof.

[0048] Embodiment 19: The process of Embodiment 17 or Embodiment 18, wherein the methanation catalysts are selected from ruthenium, cobalt, nickel or iron, and combinations thereof.

[0049] Although the foregoing description is directed to the preferred embodiments of the invention, it is noted that other variations and modifications will be apparent to those skilled in the art, and may be made without departing from the spirit or scope of the invention. Moreover, features described in connection with one embodiment of the invention may be used in conjunction with other embodiments, even if not explicitly stated above.

[0050] In general, the invention may alternately comprise, consist of, or consist essentially of, any appropriate components herein disclosed. The invention may additionally, or alternatively, be formulated so as to be devoid, or substantially free, of any components, materials, ingredients, adjuvants or species used in the prior art compositions or that are otherwise not necessary to the achievement of the function and/or objectives of the present invention. The endpoints of all ranges directed to the same component or property are inclusive and independently combinable (e.g., ranges of “less than or equal to 25 wt%, or 5 wt% to 20 wt%,” is inclusive of the endpoints and all intermediate values of the ranges of “5 wt% to 25 wt%,” etc.). Disclosure of a narrower range or more specific group in addition to

a broader range is not a disclaimer of the broader range or larger group. “Combination” is inclusive of blends, mixtures, alloys, reaction products, and the like. Furthermore, the terms “first,” “second,” and the like, herein do not denote any order, quantity, or importance, but rather are used to denote one element from another. The terms “a” and “an” and “the” herein do not denote a limitation of quantity, and are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. “Or” means “and/or.” The suffix “(s)” as used herein is intended to include both the singular and the plural of the term that it modifies, thereby including one or more of that term (e.g., the film(s) includes one or more films). Reference throughout the specification to “one embodiment”, “another embodiment”, “an embodiment”, and so forth, means that a particular element (e.g., feature, structure, and/or characteristic) described in connection with the embodiment is included in at least one embodiment described herein, and may or may not be present in other embodiments. In addition, it is to be understood that the described elements may be combined in any suitable manner in the various embodiments.

[0051] The modifier “about” used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (e.g., includes the degree of error associated with measurement of the particular quantity). The notation “ $\pm 10\%$ ” means that the indicated measurement can be from an amount that is minus 10% to an amount that is plus 10% of the stated value. The terms “front”, “back”, “bottom”, and/or “top” are used herein, unless otherwise noted, merely for convenience of description, and are not limited to any one position or spatial orientation. “Optional” or “optionally” means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where the event occurs and instances where it does not. Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this invention belongs. A “combination” is inclusive of blends, mixtures, alloys, reaction products, and the like.

[0052] All cited patents, patent applications, and other references are incorporated herein by reference in their entirety. However, if a term in the present application contradicts or conflicts with a term in the incorporated reference, the term from the present application takes precedence over the conflicting term from the incorporated reference

[0053] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or may be presently unforeseen may arise to applicants or others skilled in the art. Accordingly, the

appended claims as filed and as they may be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

[0054] I/we claim:

CLAIMS:

1. A process for producing aromatics and other chemicals, comprising:
providing methane feedstock to a first reactor to produce a first product stream comprising aromatics and hydrogen, wherein the methane feedstock is contacted with a catalyst;
recovering aromatics from the first product stream to create an aromatics depleted resulting stream;
mixing the aromatics depleted resulting stream with a feed stream to create a combined product stream; and
providing the combined product stream to a second reactor to produce a second product stream comprising water and unconverted methane.
2. The process of Claim 1, wherein the first reactor produces the first product stream by dehydroaromatization.
3. The process of Claim 1 or Claim 2, wherein the second reactor is a methanation reactor.
4. The process of any of Claims 1 to 3, wherein the aromatics are recovered from the first product stream prior to entering the second reactor.
5. The process of any of Claims 1 to 4, wherein the feed stream is selected from a carbon dioxide feed stream, a steam feed stream, and combinations thereof.
6. The process of any of Claims 1 to 5, wherein the aromatics are selected from benzene, toluene, naphthalene, other aromatics, and combinations thereof.
7. The process of any of Claims 1 to 6, wherein the catalyst is a bifunctional Zeolite supported metal catalyst.
8. The process of Claim 7, wherein the metal is selected from molybdenum, tungsten, ruthenium, iron, cobalt, nickel, copper, silver, zinc, chromium, or tin, and combinations thereof.

9. A process for producing aromatics and other chemicals from recycled methane feedstock, comprising:

receiving recycled methane from a methanation reaction;

mixing the recycled methane and methane feedstock to form a combined methane feedstock;

providing the combined methane feedstock to a first reactor to produce a first product stream comprising aromatics and hydrogen, wherein the combined methane feedstock is contacted with a catalyst;

recovering aromatics from the first product stream to create an aromatics depleted resulting stream;

mixing the aromatics depleted resulting stream with a feed stream to create a combined product stream; and

providing the combined product stream to a second reactor to produce a second product stream comprising synthetic or unconverted methane, and water.

10. The process of Claim 9, wherein the first reactor produces the first product stream by dehydroaromatization.

11. The process of Claim 9 or Claim 10, wherein the second reactor is a methanation reactor.

12. The process of any of Claims 9 to 11, wherein the carbon dioxide or steam feed stream is a carbon dioxide feed stream.

13. The process of any of Claims 9 to 12, wherein the feed stream is selected from a carbon dioxide feed stream, a steam feed stream, and combinations thereof.

14. The process of any of Claims 9 to 13, wherein the aromatics are selected from a group consisting of: benzene, toluene, naphthalene, other aromatics and combinations thereof.

15. The process of any of Claims 9 to 14, wherein the catalyst is a bifunctional Zeolite supported metal catalyst.

16. The process of any of Claims 9 to 15, wherein the metal is selected from molybdenum, tungsten, ruthenium, iron, cobalt, nickel, copper, silver, zinc, chromium, or tin, and combinations thereof.

17. A process for producing a methane-rich gas, comprising:
receiving a first resulting stream from one or more dehydroaromatization reactions;
extracting aromatics from the first resulting stream, wherein the resulting stream is converted to an aromatic depleted resulting stream;
mixing the aromatics depleted resulting stream with a carbon dioxide feed or steam feed stream to create a combined stream;
mixing the combined stream with one or more methanation catalysts in a methanation reactor to produce a second resulting stream; and
extracting water from the second resulting stream.

18. The process of Claim 17, wherein the aromatics are selected from benzene, toluene, naphthalene, other aromatics, and combinations thereof.

19. The process of Claim 17 or Claim 18, wherein the methanation catalysts are selected from ruthenium, cobalt, nickel or iron, and combinations thereof.

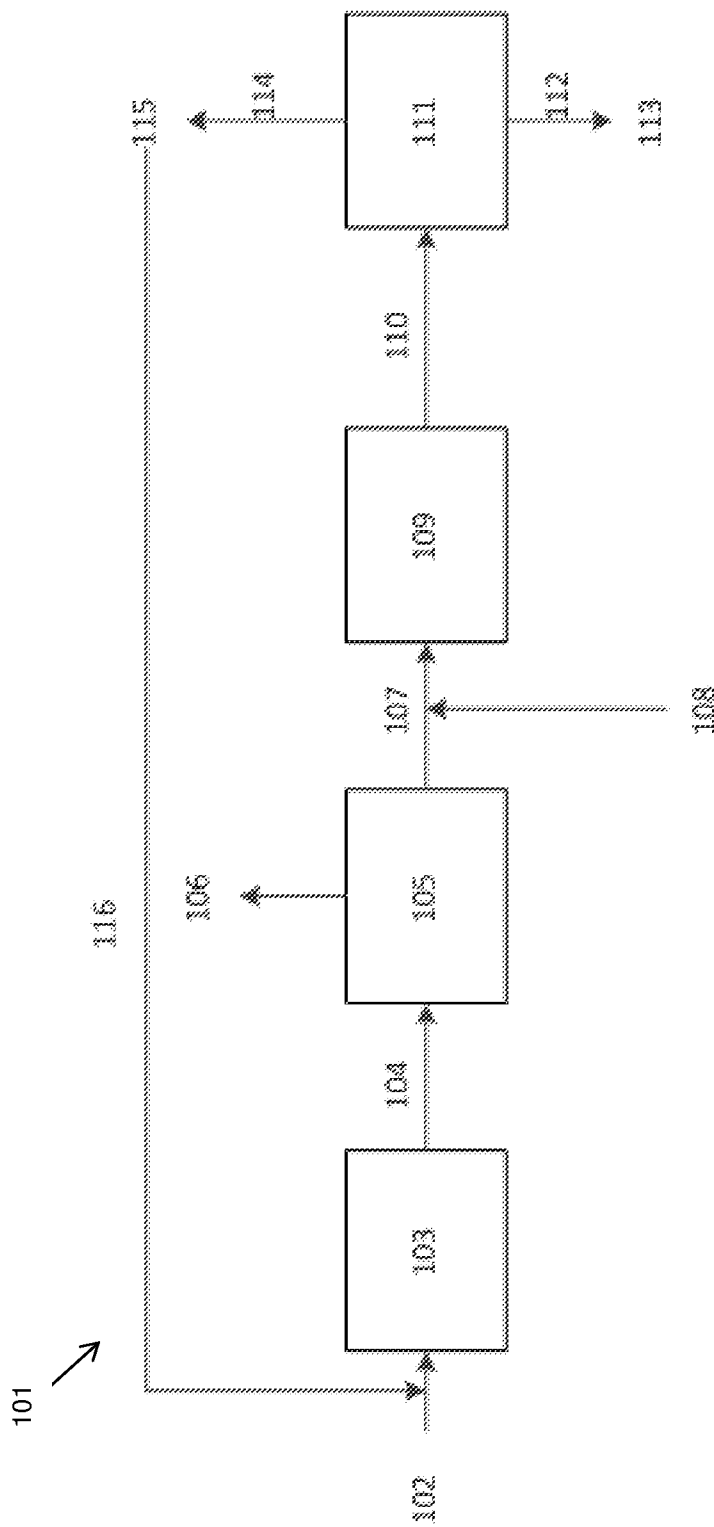


FIG. 1

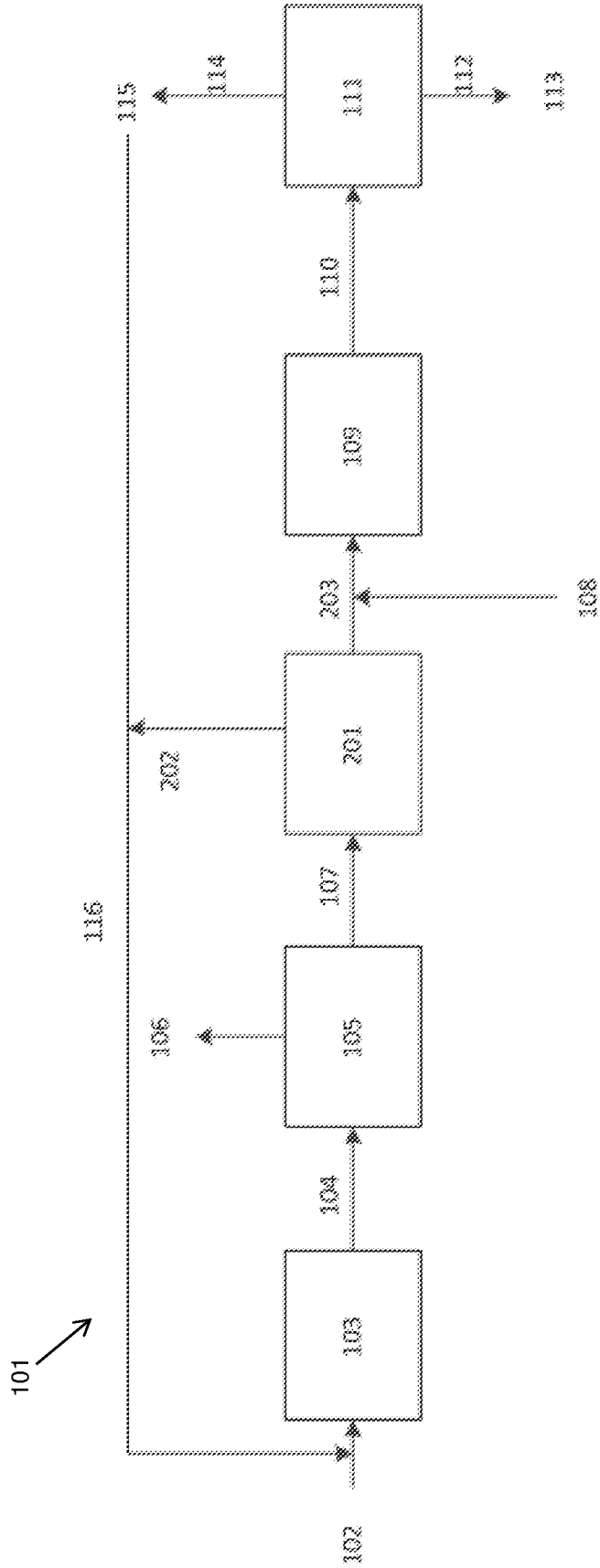


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/014735

A. CLASSIFICATION OF SUBJECT MATTER INV. C07C2/76 C07C2/84 C07C15/04 C07C15/06 C07C15/24 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C07C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2006/083409 A2 (EXXONMOBIL CHEM PATENTS INC [US]; IACCINO LARRY L [US]; STAVENS ELIZAB) 10 August 2006 (2006-08-10) figure 2; examples 2,3 -----	1-19
X	US 2007/260098 A1 (IACCINO LARRY L [US] ET AL) 8 November 2007 (2007-11-08) paragraphs [0060] - [0067], [0103] - [0105]; claim 1; figure 1 -----	1-19
☐ 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 13 April 2015	Date of mailing of the international search report 30/04/2015	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Cooper, Simon	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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