



(51) International Patent Classification:

C07C 29/15 (2006.01) C07C 31/04 (2006.01)
C07C 29/152 (2006.01)

(21) International Application Number:

PCT/IB2018/055441

(22) International Filing Date:

20 July 2018 (20.07.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/536,282 24 July 2017 (24.07.2017) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,

(54) Title: METHOD OF PRODUCING METHANOL

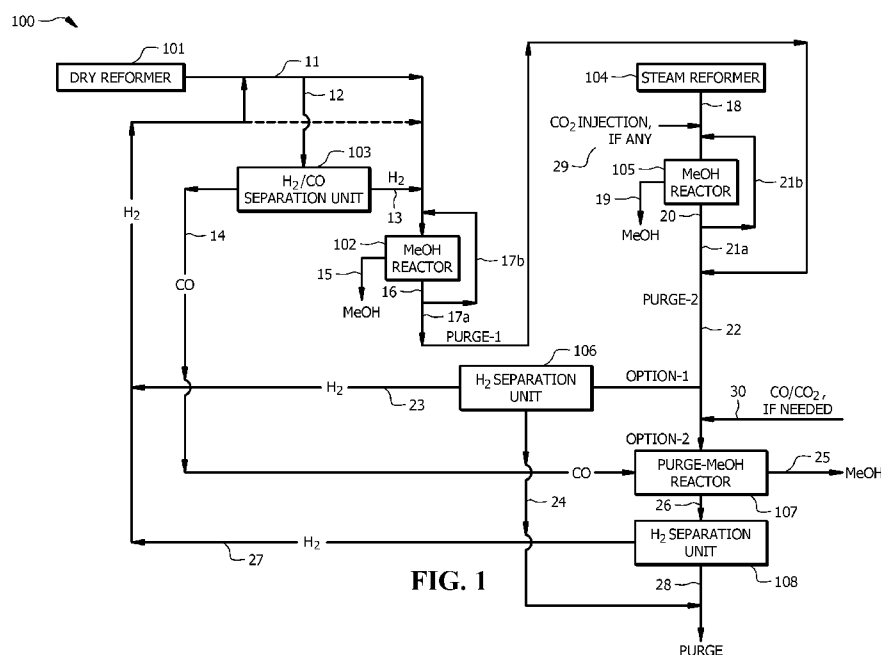


FIG. 1

(57) Abstract: Systems and methods for producing methanol with improved efficiency are disclosed. Syngas streams produced by dry reforming and by steam reforming are flowed to separate methanol synthesis reactors. A portion of the combined purge gas stream from both of the reactors is flowed to a third methanol synthesis reactor. The hydrogen from the other portion of the combined purge gas stream is separated and flowed into the syngas stream produced by dry reforming. At least some of the carbon monoxide from the syngas stream produced by dry reforming is flowed to the third methanol synthesis reactor. The hydrogen of the purge gas from the third methanol synthesis reactor is then flowed to the syngas stream produced by dry reforming. Consequently, the stoichiometric number of hydrogen to carbon monoxide (SN) flowing into each of the three methanol synthesis reactors can be maintained above 2.



SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:

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

METHOD OF PRODUCING METHANOL**CROSS REFERENCE TO RELATED APPLICATIONS**

[0001] This application claims the benefit of priority of U.S. Provisional Patent Application No. 62/536,282, filed July 24, 2017, which is hereby incorporated by reference in its entirety.

FIELD OF INVENTION

[0002] The present invention generally relates to methanol production. More specifically, the present invention relates to systems and methods for producing methanol using syngas formed by dry reforming and steam reforming processes.

BACKGROUND OF THE INVENTION

[0003] Methanol is a highly versatile chemical used in many areas of the chemical industry. First of all, it is commonly used as feedstock in manufacture of various chemicals, including plastics, paints, plywood, biodiesels, and textiles. Furthermore, methanol can also be used as a denaturant, a solvent, and an antifreeze reagent. Last but not least, many specialized vehicles have been developed to consume methanol as an alternative fuel either in combination with gasoline or alone.

[0004] Currently, the majority of methanol in the chemical industry is produced from synthesis gas (syngas), which is formed by steam reforming of methane (or natural gas). In steam reforming, steam (H_2O) reacts with methane or the methane portion of natural gas to produce hydrogen (H_2), carbon monoxide (CO) and a small amount carbon dioxide (CO_2). The main reactions in steam reforming include: $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$ and $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$. Another reaction that forms syngas is dry reforming reaction. In dry reforming, also known as carbon dioxide reforming, methane or the methane portion of natural gas reacts with carbon dioxide to produce carbon monoxide and hydrogen. The main reaction in dry reforming includes $\text{CH}_4 + \text{CO}_2 \rightleftharpoons \text{CO} + 2\text{H}_2$. In the methanol synthesis process, carbon monoxide and/or carbon dioxide react with hydrogen to produce methanol. In this process, an ideal hydrogen to carbon monoxide stoichiometric number S_N , which is defined as $[(\text{H}_2 - \text{CO}_2)/(\text{CO} + \text{CO}_2)]$, is about 2. However, the stoichiometric number of hydrogen to carbon monoxide S_N for the syngas stream produced by steam reforming is about 3, resulting in low hydrogen utilization

rate in the methanol synthesis process. In contrast, the syngas stream produced by dry reforming has a S_N of hydrogen to carbon monoxide less than 1, thereby underutilizing carbon monoxide in the methanol synthesis process. Therefore, improvements in the field are desired.

BRIEF SUMMARY OF THE INVENTION

5 **[0005]** A method has been discovered for producing methanol. The syngas streams produced from both dry reforming and steam reforming are used to produce methanol. By separating the carbon monoxide from the syngas stream produced by dry reforming, the stoichiometric number S_N of hydrogen to carbon monoxide feed to the methanol synthesis can be maintained at approximately 2, which, in turn, improves the efficiency and utilization rate
10 of the syngas. Furthermore, the carbon monoxide separated from the syngas stream produced by dry reforming may be combined with the purge gas from methanol synthesis to produce additional methanol, thereby increasing utilization rate of the syngas and maximizing the methanol synthesis efficiency.

[0006] Embodiments of the invention include a method of producing methanol. The
15 method may include dry-reforming natural gas to produce a first syngas stream comprising hydrogen, carbon monoxide, and/or carbon dioxide. At least some of the first syngas stream is flowed to a first methanol synthesis reactor. At least some of the first syngas stream is separated in a hydrogen/carbon monoxide separation unit to form a first hydrogen stream and a first carbon monoxide stream. The first hydrogen stream is then flowed to the first methanol
20 synthesis reactor. The method may further include reacting the carbon monoxide and hydrogen of the first syngas stream and the hydrogen of the first hydrogen stream in the first methanol synthesis reactor under reaction conditions sufficient to form methanol. The method may further include separating an effluent from the first methanol synthesis reactor to form a first methanol stream and a first byproduct stream. The method may further include splitting at
25 least some of the first byproduct stream to form a first purge gas stream and a first recycle stream. The method may further include steam reforming natural gas to produce a second syngas stream. The second syngas stream is flowed through a second methanol synthesis reactor. The method may further still include reacting the hydrogen, the carbon monoxide, and the carbon dioxide in the second syngas stream under reaction conditions sufficient to form
30 methanol. An effluent from the second methanol synthesis reactor may be then separated to form a second methanol stream and a second byproduct stream. The method may include splitting at least some of the second byproduct stream to form a second purge gas stream and a

second recycle stream. The first purge gas stream and the second purge gas stream may be flowed through a third methanol synthesis reactor. The first carbon monoxide stream may also be flowed to the third methanol synthesis reactor. The method may further still include reacting the hydrogen, the carbon monoxide, and/or the carbon dioxide in the third methanol synthesis reactor under reaction conditions sufficient to form at least some methanol. The methanol formed in the first methanol synthesis reactor, the second methanol synthesis reactor and the third methanol synthesis reactor is then collected.

[0007] Embodiments of the invention include a method of producing methanol. The method may include dry-reforming natural gas to produce a first syngas stream comprising hydrogen, carbon monoxide, and/or carbon dioxide. At least some of the first syngas stream is flowed to a first methanol synthesis reactor. At least some of the first syngas stream is separated in a hydrogen/carbon monoxide separation unit to form a first hydrogen stream and a first carbon monoxide stream. The first hydrogen stream is then flowed to the first methanol synthesis reactor. The method may further include reacting the carbon monoxide and the hydrogen of the first syngas stream and the hydrogen of the first hydrogen stream in the first methanol synthesis reactor under reaction conditions sufficient to form methanol. The method may further include separating an effluent from the first methanol synthesis reactor to form a first methanol stream and a first byproduct stream. The method may further include splitting at least some of the first byproduct stream to form a first purge gas stream and a first recycle stream. The method may further include steam reforming natural gas to produce a second syngas stream comprising hydrogen, carbon monoxide, and carbon dioxide. The second syngas stream is flowed through a second methanol synthesis reactor. Additional carbon dioxide may be injected into the second syngas stream. The method may further still include reacting the hydrogen, the carbon monoxide, and the carbon dioxide in the second syngas stream under reaction conditions sufficient to form at least some methanol. An effluent from the second methanol synthesis reactor may be separated to form a second methanol stream and a second byproduct stream. The method may include splitting at least some of the second byproduct stream to form a second purge gas stream and a second recycle stream. At least some of a combined stream of the first purge gas stream and the second purge gas stream collectively may be then flowed to a first hydrogen separation unit, where the first hydrogen separation unit separates the combined stream to form a second hydrogen stream and a first residue gas stream. The second hydrogen stream may be then flowed to the first syngas stream. At least some of the combined stream of the first purge gas stream and the second purge gas stream may be

flowed through a third methanol synthesis reactor. The first carbon monoxide stream may also be flowed to the third methanol synthesis reactor. The method may include injecting carbon monoxide and/or carbon dioxide, if needed, to the third methanol synthesis reactor to maintain the stoichiometric number of hydrogen to carbon monoxide flowing in the third methanol synthesis reactor equal to or greater than 2. The method may further still include reacting the hydrogen, the carbon monoxide, and/or the carbon dioxide in the third methanol synthesis reactor under reaction conditions sufficient to form methanol. The methanol formed in the first methanol synthesis reactor, the second methanol synthesis reactor and the third methanol synthesis reactor is collected.

10 **[0008]** The following includes definitions of various terms and phrases used throughout this specification.

15 **[0009]** The terms “about” or “approximately” are defined as being close to as understood by one of ordinary skill in the art. In one non-limiting embodiment the terms are defined to be within 10%, preferably, within 5%, more preferably, within 1%, and most preferably, within 0.5%.

[0010] The terms “wt.%”, “vol.%” or “mol.%” refers to a weight, volume, or molar percentage of a component, respectively, based on the total weight, the total volume, or the total moles of material that includes the component. In a non-limiting example, 10 moles of component in 100 moles of the material is 10 mol.% of component.

20 **[0011]** The term “substantially” and its variations are defined to include ranges within 10%, within 5%, within 1%, or within 0.5%.

[0012] The terms “inhibiting” or “reducing” or “preventing” or “avoiding” or any variation of these terms, when used in the claims and/or the specification, includes any measurable decrease or complete inhibition to achieve a desired result.

25 **[0013]** The term “effective,” as that term is used in the specification and/or claims, means adequate to accomplish a desired, expected, or intended result.

[0014] The term “stoichiometric number of hydrogen to carbon monoxide” or “ S_N ” as that term is used in the specification and/or claims, refers to a ratio of $[(H_2 - CO_2)/(CO + CO_2)]$, where $(H_2 - CO_2)$ is the molar concentration difference between hydrogen and carbon dioxide

in a mixture or a stream, and $(\text{CO} + \text{CO}_2)$ is the molar concentration sum between carbon monoxide and carbon dioxide in a mixture or a stream.

[0015] The term “primarily” as used herein means greater than 50%, e.g., 51 to 99%, based on the measure, e.g., weight %, volume %, etc.

5 **[0016]** The use of the words “a” or “an” when used in conjunction with the term “comprising,” “including,” “containing,” or “having” in the claims or the specification may mean “one,” but it is also consistent with the meaning of “one or more,” “at least one,” and “one or more than one.”

10 **[0017]** The words “comprising” (and any form of comprising, such as “comprise” and “comprises”), “having” (and any form of having, such as “have” and “has”), “including” (and any form of including, such as “includes” and “include”) or “containing” (and any form of containing, such as “contains” and “contain”) are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

15 **[0018]** The process of the present invention can “comprise,” “consist essentially of,” or “consist of” particular ingredients, components, compositions, etc., disclosed throughout the specification.

[0019] In the context of the present invention at least 16 embodiments are now described. Embodiment 1 is a method of producing methanol. The method includes the steps of dry-reforming natural gas to produce a first syngas stream containing hydrogen, carbon
20 monoxide, and/or carbon dioxide; flowing at least some of the first syngas stream to a first methanol synthesis reactor; separating at least some of the first syngas stream in a hydrogen/carbon monoxide separation unit to form a first hydrogen stream and a first carbon monoxide stream; flowing the first hydrogen stream to the first methanol synthesis reactor; reacting the carbon monoxide and/or carbon dioxide of the first syngas stream with hydrogen
25 of the first hydrogen stream and the hydrogen of the first syngas stream in the first methanol synthesis reactor under reaction conditions sufficient to form methanol; separating an effluent from the first methanol synthesis reactor to form a first methanol stream and a first byproduct stream; splitting at least some of the first byproduct stream to form a first purge gas stream and a first recycle stream; steam reforming natural gas to produce a second syngas stream
30 containing hydrogen, carbon monoxide, and carbon dioxide; flowing the second syngas stream through a second methanol synthesis reactor; reacting the hydrogen, the carbon monoxide, and

the carbon dioxide in the second syngas stream in the second methanol synthesis reactor under reaction conditions sufficient to form methanol; separating an effluent from the second methanol synthesis reactor to form a second methanol stream and a second byproduct stream; splitting at least some of the second byproduct stream to form a second purge gas stream and a second recycle stream; flowing a combined stream of the first purge gas stream and the second purge gas stream through a third methanol synthesis reactor, wherein the combined stream contains primarily hydrogen, carbon monoxide, and/or carbon dioxide; flowing the first carbon monoxide stream to the third methanol synthesis reactor; and reacting the hydrogen in the third methanol synthesis reactor with carbon monoxide and/or carbon dioxide in the third methanol synthesis reactor under reaction conditions sufficient to form methanol and a third purge gas stream. Embodiment 2 is the method of embodiment 1, wherein the hydrogen, the carbon monoxide and the carbon dioxide flowing in each of the first methanol synthesis reactor, the second methanol synthesis reactor and the third methanol synthesis reactor has a stoichiometric number of hydrogen to carbon monoxide (SN) equal to or greater than 2. Embodiment 3 is the method of any of embodiments 1 and 2, further including the step of injecting carbon dioxide into the second syngas stream. Embodiment 4 is the method of any of embodiments 1 to 3, further including the step of injecting carbon monoxide and/or carbon dioxide to the third methanol synthesis reactor to maintain the stoichiometric number of hydrogen to carbon monoxide (SN) no less than 2. Embodiment 5 is the method of any of embodiments 1 to 4, further including the step of flowing at least some of the combined stream of the first purge gas stream and the second purge gas stream to a first hydrogen separation unit; separating the combined stream to form a second hydrogen stream and a first residue gas stream via the first hydrogen separation unit; and flowing the second hydrogen stream to the first syngas stream. Embodiment 6 is the method of any of embodiments 1 to 5, further including the step of flowing the third purge gas stream to a second hydrogen separation unit; separating the third purge gas stream to form a third hydrogen stream and a second residue gas stream; and flowing the third hydrogen stream to the first syngas stream. Embodiment 7 is the method of embodiment 6, wherein the third purge gas stream contains CO, CO₂, H₂, CH₄, or combinations thereof. Embodiment 8 is the method of any of embodiments 1 to 7, wherein the reaction conditions in each of the methanol synthesis reactors include a reaction temperature in a range of 200 °C to 300 °C. Embodiment 9 is the method of any of embodiments 1 to 8, wherein the reaction conditions in each of the methanol synthesis reactors include a reaction pressure of 50 bar to 100 bar. Embodiment 10 is the method of any of embodiments 1 to 9, wherein the reacting in each of the methanol synthesis reactors is performed in the presence of

a catalyst selected from the group consisting of copper and zinc supported on alumina, chromium and manganese oxide, and combinations thereof. Embodiment 11 is the method of any of embodiments 1 to 10, wherein the reaction conditions in each of the methanol synthesis reactors include a gas hourly space velocity in a range of 8000 per hour to 10000 per hour.

- 5 Embodiment 12 is the method of any of embodiments 1 to 11, wherein the first purge gas stream and the second purge gas stream contain H_2 , CO, CO_2 , CH_4 , or combinations thereof. Embodiment 13 is the method of any of embodiments 1 to 12, further including the step of recycling the first recycle stream to the first methanol synthesis reactor, wherein the first recycle stream contains unreacted hydrogen, unreacted carbon monoxide, and unreacted carbon
- 10 dioxide. Embodiment 14 is the method of any of embodiments 1 to 13, further including the step of recycling the second recycle stream to the second methanol synthesis reactor, wherein the second recycle stream contains unreacted hydrogen, unreacted carbon monoxide, and unreacted carbon dioxide.

- [0020]** Embodiment 15 is a method of producing methanol, the method including the
- 15 step of dry-reforming natural gas to produce a first syngas stream containing hydrogen, carbon monoxide, and/or carbon dioxide; flowing at least some of the first syngas stream to a first methanol synthesis reactor; separating at least some of the first syngas stream via a hydrogen/carbon monoxide separation unit to form a first hydrogen stream and a first carbon monoxide stream; flowing the first hydrogen stream to the first methanol synthesis reactor;
- 20 reacting the carbon monoxide and/or carbon dioxide of the first syngas stream with the hydrogen of the first hydrogen stream and the hydrogen of the first syngas stream in the first methanol synthesis reactor under reaction conditions sufficient to form methanol; separating an effluent from the first methanol synthesis reactor to form a first methanol stream and a first byproduct stream; splitting at least some of the first byproduct stream to form a first purge gas
- 25 stream and a first recycle stream; steam reforming natural gas to produce a second syngas stream containing hydrogen, carbon monoxide, and carbon dioxide; flowing the second syngas stream through a second methanol synthesis reactor; injecting carbon dioxide and/or carbon monoxide to the second syngas stream to ensure a stoichiometric number of hydrogen to carbon monoxide (SN) flowing into the second methanol synthesis in a range of 2 to 2.1; reacting the
- 30 hydrogen, the carbon monoxide, and the carbon dioxide in the second syngas stream in the second methanol synthesis reactor under reaction conditions sufficient to form methanol; separating an effluent from the second methanol synthesis reactor to form a second methanol stream and a second byproduct stream; splitting at least some of the second byproduct stream

to form a second purge gas stream and a second recycle stream; flowing at least some of a combined stream of the first purge gas stream and the second purge gas stream through a first hydrogen separation unit to form a second hydrogen stream and a first residue gas stream; flowing the second hydrogen stream to the first syngas stream; flowing at least some of the combined stream of the first purge gas stream and the second purge gas stream through a third methanol synthesis reactor, wherein the combined stream contains primarily hydrogen, carbon monoxide, and/or carbon dioxide; flowing the first carbon monoxide stream to the third methanol synthesis reactor; injecting carbon monoxide and/or carbon dioxide to the third methanol synthesis reactor; reacting the hydrogen in the third methanol synthesis reactor with carbon monoxide and/or carbon dioxide in the third methanol synthesis reactor under reaction conditions sufficient to form methanol and a third purge gas stream; flowing the third purge gas stream to a second hydrogen separation unit; separate the third purge gas stream in the second hydrogen separation unit to form a third hydrogen stream and a second residue stream; and flowing the third hydrogen stream to the first syngas stream. Embodiment 16 is the method of embodiment 15, wherein the first syngas stream flowing in the first methanol synthesis reactor and the second syngas stream flowing in the second methanol synthesis reactor each has a stoichiometric number of hydrogen to carbon monoxide (SN) equal to or greater than 2.

[0021] Other objects, features and advantages of the present invention will become apparent from the following figures, detailed description, and examples. It should be understood, however, that the figures, detailed description, and examples, while indicating specific embodiments of the invention, are given by way of illustration only and are not meant to be limiting. Additionally, it is contemplated that changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description. In further embodiments, features from specific embodiments may be combined with features from other embodiments. For example, features from one embodiment may be combined with features from any of the other embodiments. In further embodiments, additional features may be added to the specific embodiments described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] For a more complete understanding, reference is now made to the following descriptions taken in conjunction with the accompanying drawings, in which:

[0023] FIG. 1 shows a schematic diagram of a system for producing methanol, according to embodiments of the invention; and

[0024] FIG. 2 shows a schematic flowchart for a method of producing methanol, according to embodiments of the invention.

5

DETAILED DESCRIPTION OF THE INVENTION

[0025] A method has been discovered for producing methanol using syngas streams produced by both dry reforming and steam reforming of methane. The first syngas stream is produced by dry reforming and then flowed to a first methanol synthesis reactor, and the second syngas stream is produced by steam reforming and then flowed to a second methanol synthesis reactor. The carbon monoxide produced in the first syngas stream is redistributed to the combined purge gas stream from both methanol synthesis reactors. At least some of the hydrogen from the combined purge gas stream is separated and recycled to the first syngas stream. Thus, the stoichiometric number of hydrogen to carbon monoxide feeding to the first methanol reactor may be maintained at approximately 2, improving the utilization rate of the hydrogen and carbon monoxide. By further reacting the hydrogen, carbon monoxide, and/or carbon dioxide of the combined purge gas stream in a third methanol synthesis reactor, additional methanol is formed, thereby maximizing the utilization rate of hydrogen and carbon monoxide produced by both dry reforming and steam reforming of methane.

[0026] With reference to FIG. 1, a schematic diagram is shown of methanol production system 100, according to embodiments of the invention. Methanol production system 100 may comprise dry reformer 101 that is configured to react methane with carbon dioxide to form syngas stream 11 comprising primarily hydrogen, carbon monoxide, and/or carbon dioxide, collectively. An outlet of dry reformer 101 may be in fluid communication with first methanol synthesis reactor 102.

[0027] According to embodiments of the invention, the outlet of dry reformer 101 may be in fluid communication with hydrogen/carbon monoxide separation unit 103, which is configured to separate at least some of first syngas stream 11 (split syngas stream 12) into first hydrogen stream 13 and first carbon monoxide stream 14. In embodiments of the invention, hydrogen/carbon monoxide separation unit 103 may include pressure swing adsorption unit, membrane separation unit, or combinations thereof. The outlet of hydrogen/carbon monoxide

separation unit 103 for first hydrogen stream 13 may be in fluid communication with first methanol synthesis reactor 102.

[0028] In embodiments of the invention, an effluent separator may be installed downstream to first methanol synthesis reactor 102. The effluent separator may be configured to separate an effluent from first methanol synthesis reactor 102 into first methanol stream 15 and first byproduct stream 16. A splitter may be used to split first byproduct stream 16 to form first purge gas stream 17a and first recycle stream 17b. According to embodiments of the invention, first purge gas stream 17a may comprise hydrogen, CH₄, CO, CO₂, or combinations thereof.

[0029] According to embodiments of the invention, methanol production system 100 may further include steam reformer 104, configured to react steam with methane to form second syngas stream 18, which comprises hydrogen, carbon monoxide, and a small amount of carbon dioxide (typically 2.0 vol.% to 6.0 vol.%). An outlet of steam reformer 104 is in fluid communication with second methanol synthesis reactor 105. According to embodiments of the invention, an effluent separator may be installed downstream to second methanol synthesis reactor 105. The effluent separator may be configured to separate the effluent from second methanol synthesis reactor 105 into second methanol stream 19 and second byproduct stream 20. A splitter may be used to split at least some of second byproduct stream 20 to form second purge gas stream 21a and second recycle stream 21b. In embodiments of the invention, second purge gas stream 21a may include hydrogen, CH₄, CO, CO₂ or combinations thereof. First purge gas stream 17a may be combined with second purge gas stream 21a to form combined purge gas stream 22.

[0030] In embodiments of the invention, combined purge gas stream may be configured to flow to first hydrogen separation unit 106. First hydrogen separation unit 106 may be configured to separate at least some combined purge gas stream 22 into second hydrogen stream 23 and first residue gas stream 24. First hydrogen separation unit 106 may comprise a hydrogen outlet in fluid communication with first syngas stream 11, such that methanol production system 100 is configured to flow second hydrogen stream 23 to first syngas stream 11 and subsequently first methanol synthesis reactor 102. In embodiments of the invention, first hydrogen separation unit 106 may include pressure swing adsorption unit, membrane separation unit, or combinations thereof.

[0031] According to embodiments of the invention, methanol production system 100 may further include third methanol synthesis reactor 107 configured to receive at least some of combined purge gas stream 22 and/or first carbon monoxide stream 14 from hydrogen/carbon monoxide separation unit 103. Third methanol synthesis reactor 107 may be configured to react the hydrogen from combined purge gas stream 22 with carbon monoxide from first carbon monoxide stream 14 and/or combined purge stream 22 to form methanol in third methanol stream 25. Third methanol synthesis reactor 107 may comprise an outlet in fluid communication with second hydrogen separation unit 108 configured to flow third purge gas stream 26 to second hydrogen separation unit 108. Second hydrogen separation unit 108 may be configured to separate third purge gas stream 26 into third hydrogen stream 27 and second residue gas stream 28. Third hydrogen stream 27 may be in fluid communication with first syngas stream 11. In embodiments of the invention, examples of second hydrogen separation unit 108 may include, but are not limited to pressure swing adsorption unit, membrane separation unit, or combinations thereof.

[0032] In embodiments of the invention, methanol production system 100 may comprise a control system configured to control flow rates of split syngas stream 12 flowing to hydrogen/carbon monoxide separation unit 103. The control system may further be configured to control the flow rate and/or flow rate ratio of first purge gas stream 17a to first recycle stream 17b and the flow rate and/or flow rate ratio of second purge gas stream 21a to second recycle stream 21b. The control system may further be configured to control a flow rate and/or flow rate ratio of the portion of combined purge gas stream 22 flowing to first hydrogen separation unit 106 to the portion of combined purge gas stream 22 flowing to third methanol synthesis reactor 107. The control system may further still be configured to control a flow rate of additional carbon dioxide stream 29 injected to second methanol synthesis reactor 105, and a flow rate of additional carbon dioxide/carbon monoxide stream 30 injected to third methanol synthesis reactor 107. Overall, according to embodiments of the invention, the control system ensures that the hydrogen, the carbon monoxide, and/or the carbon dioxide flowing in each of first methanol synthesis reactor 102, second methanol synthesis reactor 105, and third methanol synthesis reactor 107 has a stoichiometric number of hydrogen to carbon monoxide of at least 2, preferably, in a range of 2.0 to 2.1 and all ranges and values there between.

[0033] As shown in FIG. 2, embodiments of the invention include method 200 of producing methanol. Method 200 may be implemented by methanol production system 100 as

shown in FIG. 1. According to embodiments of the invention, method 200 may include dry-reforming natural gas to produce first syngas stream 11 in dry reformer 101, as shown in block 201. In embodiments of the invention, the natural gas comprises primarily methane. The dry-reforming may be performed at a reaction temperature of 850 to 950 °C and all ranges and values there between, including 860 °C, 870 °C, 880 °C, 890 °C, 900 °C, 910 °C, 920 °C, 930 °C, and 940 °C. The dry-reforming may be performed at a reaction pressure of 1 to 20 bar and all ranges and values there between including 2 bar, 3 bar, 4 bar, 5 bar, 6 bar, 7 bar, 8 bar, 9 bar, 10 bar, 11 bar, 12 bar, 13 bar, 14 bar, 15 bar, 16 bar, 17 bar, 18 bar, 19 bar. First syngas stream 11 may comprise 30 to 50 vol.% hydrogen, 40 to 50 vol.% carbon monoxide, and 1 to 6 vol.% carbon dioxide. The specific composition of first syngas stream 11 may be dependent on the reaction pressure for the dry-reforming. Typically, the dry-reforming may have a conversion rate of methane in a range of 50 to 95% and all ranges and values there between including ranges of 50 to 55%, 55 to 60%, 60 to 65%, 65 to 70%, 70 to 75%, 75 to 80%, 80 to 85%, 85 to 90%, and 90 to 95%. The exact conversion rate of methane may be dependent on the reaction pressure.

[0034] According to embodiments of the invention, first syngas stream 11 from dry reformer 101 may comprise primarily hydrogen and carbon monoxide, collectively. First syngas stream 11 may further include carbon dioxide. An stoichiometric number (S_N) of hydrogen to carbon monoxide for typical syngas produced by dry reformer 101 is less than 1. S_N is defined as $[(H_2 - CO_2)/(CO + CO_2)]$, where $(H_2 - CO_2)$ is the molar concentration difference between hydrogen and carbon dioxide and $(CO + CO_2)$ is the molar concentration sum between carbon monoxide and carbon dioxide.

[0035] As shown in block 202, method 200 may further include flowing at least some of first syngas stream 11 to first methanol synthesis reactor 102. Further, block 203 shows that method 200 may include flowing at least some of first syngas stream 11 (split syngas stream 12) to hydrogen/carbon monoxide separation unit 103, where split syngas stream 12 is separated to form first hydrogen stream 13 and first carbon monoxide stream 14. First hydrogen stream 13 then may be flowed to first methanol synthesis reactor 102, as shown in block 204. According to embodiments of the invention, flowing first hydrogen stream 13 as described in block 204 may include injecting first hydrogen stream 13 into first syngas stream 11 upstream or downstream to the flowing at least some of first syngas stream 11 (split syngas stream 12) at block 203. In embodiments of the invention, the hydrogen, the carbon monoxide

and/or the carbon dioxide flowing to first methanol synthesis reactor 102 may have a stoichiometric number S_N no less than 2. Preferably, the stoichiometric number may be maintained in a range of 2 to 2.1 and all ranges and values there between.

[0036] In embodiments of the invention, as shown in block 205, method 200 may further comprise reacting the carbon monoxide and/or carbon dioxide of first syngas stream 11 with the hydrogen of first hydrogen stream 13 and the hydrogen of first syngas stream 11 in first methanol synthesis reactor 102, under reaction conditions sufficient to form at least some methanol. In embodiments of the invention, the reaction conditions at block 205 may include a reaction temperature in a range of 200 °C to 300 °C and all ranges and values there between including ranges of 200 °C to 205 °C, 205 °C to 210 °C, 210 °C to 215 °C, 215 °C to 220 °C, 220 °C to 225 °C, 225 °C to 230 °C, 230 °C to 235 °C, 235 °C to 240 °C, 240 °C to 245 °C, 245 °C to 250 °C, 250 °C to 255 °C, 255 °C to 260 °C, 260 °C to 265 °C, 265 °C to 270 °C, 270 °C to 275 °C, 275 °C to 280 °C, 280 °C to 285 °C, 285 °C to 290 °C, 290 °C to 295 °C, or 295 °C to 300 °C.

[0037] In embodiments of the invention, the reaction conditions at block 205 may include a reaction pressure of 50 bar to 100 bar and all ranges and values there between, including ranges of 50 bar to 55 bar, 55 bar to 60 bar, 60 bar to 65 bar, 65 bar to 70 bar, 70 bar to 75 bar, 75 bar to 80 bar, 80 bar to 85 bar, 85 bar to 90 bar, 90 bar to 95 bar, or 95 bar to 100 bar. According to embodiments of the invention, the reacting in block 205 may be performed in the presence of a catalyst. The catalyst may include a metal, a metal oxide, or combinations thereof. Exemplary catalysts may include copper and/or zinc supported on alumina, chromium and manganese oxide, and combinations thereof. In embodiments of the invention, the reaction conditions may include a gas space velocity of 8000 to 10000 per hour and all ranges and values there between, including 8100 per hour, 8200 per hour, 8300 per hour, 8400 per hour, 8500 per hour, 8600 per hour, 8700 per hour, 8800 per hour, 8900 per hour, 9000 per hour, 9100 per hour, 9200 per hour, 9300 per hour, 9400 per hour, 9500 per hour, 9600 per hour, 9700 per hour, 9800 per hour, and 9900 per hour.

[0038] In embodiments of the invention, an effluent from first methanol synthesis reactor 102 may comprise methanol, unreacted hydrogen, unreacted carbon monoxide, and unreacted carbon dioxide. According to embodiments of the invention, the effluent from first methanol synthesis reactor 102 may be separated to form first methanol stream 15 and first byproduct stream 16 as shown in block 206. Block 207 shows that method 200 may include

splitting at least some of first byproduct stream 16 to form first purge gas stream 17a and first recycle stream 17b. First recycle stream 17b may be recycled back to first methanol synthesis reactor 102. In embodiments of the invention, the splitting in block 207 may be configured to control the hydrogen content flowing in first methanol synthesis reactor 102. According to
5 embodiments of the invention, first byproduct stream 16, first purge gas stream 17a, and first recycle stream 17b each may include unreacted hydrogen, unreacted carbon monoxide, and unreacted carbon dioxide. In general, the conversion rate of hydrogen in block 205 may be in a range of 12% to 19%, whereas the conversion rate of carbon monoxide is about 66% to 77% and carbon dioxide in the reaction has a conversion rate of 40% to 45%. This results in a high
10 hydrogen content in first byproduct stream 16 and in first methanol synthesis reactor 102. Thus, first purge gas stream 17a may comprise primarily hydrogen at a concentration as high as 90 vol.%. First purge gas stream 17a may further comprise 2 vol.% carbon monoxide and/or 1 vol.% carbon dioxide.

[0039] In embodiments of the invention, as shown in block 208, method 200 may
15 further comprise steam reforming natural gas in steam reformer 104 to produce second syngas stream 18. The steam reforming may be performed at a reaction temperature of 850 to 900 °C and all ranges and values there between including ranges of 850 to 860 °C, 860 to 870 °C, 870 to 880 °C, 880 to 890 °C, and 890 to 900 °C. The steam reforming may be performed at a reaction pressure of 1 to 25 bar and all ranges and values there between including 2 bar, 3 bar,
20 4 bar, 5 bar, 6 bar, 7 bar, 8 bar, 9 bar, 10 bar, 11 bar, 12 bar, 13 bar, 14 bar, 15 bar, 16 bar, 17 bar, 18 bar, 19 bar, 20 bar, 21 bar, 22 bar, 23 bar, and 24 bar. Typically, the steam reforming may have a conversion rate of methane in a range of 80 to 86% and all ranges and values there between including 81%, 82%, 83%, 84%, and 85%. Second syngas stream 18 may comprise 73 to 74 vol. % hydrogen, 16 to 17 vol. % carbon monoxide, and 6 to 7 vol.% carbon dioxide.
25 According to embodiments of the invention, carbon dioxide of additional carbon dioxide stream 29 may be injected in second syngas stream 18, such that the hydrogen, the carbon monoxide, the carbon dioxide flowing in second methanol synthesis reactor 105 have a stoichiometric number S_N of no less than 2, preferably, 2 to 2.1.

[0040] As shown in block 209, second syngas stream 18 is flowed to second methanol
30 synthesis reactor 105. Method 200 may further include reacting the hydrogen, the carbon monoxide, and the carbon dioxide of second syngas stream 18 in second methanol synthesis reactor 105 under reaction conditions sufficient to form at least some methanol as shown in

block 210. In embodiments of the invention, the reaction conditions at block 210 may be substantially the same as reaction conditions at block 205, which include a reaction temperature of 200 °C to 300 °C, a reaction pressure of 50 bar to 100 bar, and a gas hourly space velocity of 8000 to 10000 per hour. Similar to block 205, the reacting in block 210 may be performed in the presence of a catalyst. The catalyst may include a metal, a metal oxide, or combinations thereof. Exemplary catalysts may include copper and/or zinc supported on alumina, chromium and manganese oxide, and combinations thereof.

[0041] In embodiments of the invention, as shown in block 211, the effluent from second methanol synthesis reactor 105 may be separated to form second methanol stream 19 and second byproduct stream 20. Block 212 shows that at least some of second byproduct stream 20 may be split to form second purge gas stream 21a and second recycle stream 21b. Second recycle stream 21b may be recycled back to second methanol synthesis reactor 105. According to embodiments of the invention, second byproduct stream 20, second purge gas stream 21a, and second recycle stream 21b each may comprise unreacted hydrogen, unreacted carbon monoxide, and unreacted carbon dioxide. The hydrogen content in second purge gas stream 21a may be in a range of 80 to 90 vol.% without CO₂ injection. In embodiments of the invention, second purge gas stream 21a may be configured to reduce the hydrogen content in second recycle stream 21b and in second methanol synthesis reactor 105. According to embodiments of the invention, first purge gas stream 17a and second purge gas stream 21a may be combined to form combined purge gas stream 22. As shown in block 213, combined purge gas stream 22 may be flowed through third methanol synthesis reactor 107. Block 214 shows that first carbon monoxide stream 14 from hydrogen/carbon monoxide separation unit 103 may be flowed through third methanol synthesis reactor 107. Further, in embodiments of the invention, additional carbon monoxide and/or carbon dioxide of stream 30 may be injected in third methanol synthesis reactor 107. The additional carbon monoxide and/or carbon dioxide of stream 30 may be configured to maintain the stoichiometric number of hydrogen to carbon monoxide (S_N) for the hydrogen, the carbon monoxide and the carbon dioxide flowing in third methanol synthesis reactor 107 equal to or greater than 2, preferably 2 to 2.1. According to embodiments of the invention, as shown in block 215, method 200 may further include reacting the hydrogen with carbon monoxide and/or carbon dioxide in third methanol synthesis reactor 107 under reaction conditions sufficient to form methanol in third methanol stream 25 and third purge gas stream 26.

[0042] Similar to the reacting in blocks 205 and 210, in embodiments of the invention, reaction conditions in block 215 may include a reaction temperature of 200 °C to 300 °C, a reaction pressure of 50 bar to 100 bar, and a gas hourly space velocity of 80000 to 10000 per hour. Similar to blocks 205 and 210, the reacting in block 215 may be performed in the presence of a catalyst. The catalyst may include a metal, a metal oxide, or combinations thereof. Exemplary catalysts may include, but are not limited to, copper and/or zinc supported on alumina, chromium and manganese oxide, and combinations thereof.

[0043] In embodiments of the invention, methanol may be collected from first methanol stream 15, second methanol stream 19 and third methanol stream 25, as shown in block 216. Third purge gas stream 26, according to embodiments of the invention, may be flowed to second hydrogen separation unit 108, where third purge gas stream 26 is separated to form third hydrogen stream 27 and second residue gas stream 28, as shown in block 217. In embodiments of the invention, second residue gas stream 28 may be enriched with hydrogen and methane. As shown in block 218, third hydrogen stream 27 may be flowed into first syngas stream 11.

[0044] As an alternative to, or in addition to flowing combined purge gas stream 22 to third methanol synthesis reactor 107, at least some of combined purge gas stream 22 may be flowed to first hydrogen separation unit 106, where at least some of combined purge gas stream 22 is separated to form second hydrogen stream 23 and first residue gas stream 24 as shown in block 219. According to embodiments of the invention, second hydrogen stream 23 may be flowed into first syngas stream 11, as shown in block 220. First hydrogen stream 13, second hydrogen stream 23 and third hydrogen stream 27 may increase the stoichiometric number S_N of hydrogen to carbon monoxide for first syngas stream 11 to more than 2, preferably 2 to 2.1. In embodiments of the invention, first residue gas stream 24 may include carbon monoxide, carbon dioxide, and/or hydrogen. First residue gas stream 24 may be combined with second residue gas stream 28.

[0045] In summary, embodiments of the invention involve systems and methods for producing methanol with improved efficiency and utilization rate of syngas. Each of the syngas stream from dry reforming and syngas stream from steam reforming is flowed to a separate methanol synthesis reactor. At least some of the combined purge gas stream from the two methanol reactors is flowed to the third methanol synthesis reactor. Further, by feeding the syngas stream formed by dry reforming with the hydrogen separated from the combined purge

gas stream and the purge gas stream of the third methanol synthesis reactor, the stoichiometric number S_N for syngas stream formed by dry reforming increases. Moreover, by separating at least some carbon monoxide from the syngas stream formed by dry reforming and feeding the separated carbon monoxide to the third methanol synthesis reactor, the stoichiometric number S_N for syngas stream formed by dry reforming can be maintained above 2. The utilization rate for carbon monoxide can also be increased.

[0046] Although embodiments of the present invention have been described with reference to blocks of FIG. 2, it should be appreciated that operation of the present invention is not limited to the particular blocks and/or the particular order of the blocks illustrated in FIG. 2. Accordingly, embodiments of the invention may provide functionality as described herein using various blocks in a sequence different than that of FIG. 2.

[0047] Although embodiments of the present application and their advantages have been described in detail, it should be understood that various changes, substitutions and alterations can be made herein without departing from the spirit and scope of the embodiments as defined by the appended claims. Moreover, the scope of the present application is not intended to be limited to the particular embodiments of the process, machine, manufacture, composition of matter, means, methods and steps described in the specification. As one of ordinary skill in the art will readily appreciate from the above disclosure, processes, machines, manufacture, compositions of matter, means, methods, or steps, presently existing or later to be developed that perform substantially the same function or achieve substantially the same result as the corresponding embodiments described herein may be utilized. Accordingly, the appended claims are intended to include within their scope such processes, machines, manufacture, compositions of matter, means, methods, or steps.

CLAIMS

1. A method of producing methanol, the method comprising:
 - dry-reforming natural gas to produce a first syngas stream comprising hydrogen, carbon monoxide, and/or carbon dioxide;
 - flowing at least some of the first syngas stream to a first methanol synthesis reactor;
 - separating at least some of the first syngas stream in a hydrogen/carbon monoxide separation unit to form a first hydrogen stream and a first carbon monoxide stream;
 - flowing the first hydrogen stream to the first methanol synthesis reactor;
 - reacting the carbon monoxide and/or carbon dioxide of the first syngas stream with hydrogen of the first hydrogen stream and the hydrogen of the first syngas stream in the first methanol synthesis reactor under reaction conditions sufficient to form methanol;
 - separating an effluent from the first methanol synthesis reactor to form a first methanol stream and a first byproduct stream;
 - splitting at least some of the first byproduct stream to form a first purge gas stream and a first recycle stream;
 - steam reforming natural gas to produce a second syngas stream comprising hydrogen, carbon monoxide, and carbon dioxide;
 - flowing the second syngas stream through a second methanol synthesis reactor;
 - reacting the hydrogen, the carbon monoxide, and the carbon dioxide in the second syngas stream in the second methanol synthesis reactor under reaction conditions sufficient to form methanol;
 - separating an effluent from the second methanol synthesis reactor to form a second methanol stream and a second byproduct stream;
 - splitting at least some of the second byproduct stream to form a second purge gas stream and a second recycle stream;
 - flowing a combined stream of the first purge gas stream and the second purge gas stream through a third methanol synthesis reactor, wherein the combined stream comprises primarily hydrogen, carbon monoxide, and/or carbon monoxide;
 - flowing the first carbon monoxide stream to the third methanol synthesis reactor;
- and

reacting the hydrogen in the third methanol synthesis reactor with carbon monoxide and/or carbon dioxide in the third methanol synthesis reactor under reaction conditions sufficient to form methanol and a third purge gas stream.

2. The method of claim 1, wherein the hydrogen, the carbon monoxide and the carbon dioxide flowing in each of the first methanol synthesis reactor, the second methanol synthesis reactor and the third methanol synthesis reactor has a stoichiometric number of hydrogen to carbon monoxide (S_N) equal to or greater than 2.
3. The method of any of claims 1 and 2, further comprising injecting carbon dioxide into the second syngas stream.
4. The method of any of claims 1 and 2, further comprising injecting carbon monoxide and/or carbon dioxide to the third methanol synthesis reactor to maintain the stoichiometric number of hydrogen to carbon monoxide (S_N) no less than 2.
5. The method of any of claims 1 and 2, further comprising:
flowing at least some of the combined stream of the first purge gas stream and the second purge gas stream to a first hydrogen separation unit;
separating the combined stream to form a second hydrogen stream and a first residue gas stream via the first hydrogen separation unit; and
flowing the second hydrogen stream to the first syngas stream.
6. The method of any of claims 1 and 2, further comprising:
flowing the third purge gas stream to a second hydrogen separation unit;
separating the third purge gas stream to form a third hydrogen stream and a second residue gas stream; and
flowing the third hydrogen stream to the first syngas stream.
7. The method of claim 6, wherein the third purge gas stream comprises CO, CO₂, H₂, CH₄, or combinations thereof.
8. The method of any of claims 1 and 2, wherein the reaction conditions in each of the methanol synthesis reactors include a reaction temperature in a range of 200 °C to 300 °C.

9. The method of any of claims 1 and 2, wherein the reaction conditions in each of the methanol synthesis reactors include a reaction pressure of 50 bar to 100 bar.
10. The method of any of claims 1 and 2, wherein the reacting in each of the methanol synthesis reactors is performed in the presence of a catalyst selected from the group consisting of copper and zinc supported on alumina, chromium and manganese oxide, and combinations thereof.
11. The method of any of claims 1 and 2, wherein the reaction conditions in each of the methanol synthesis reactors comprise a gas hourly space velocity in a range of 8000 per hour to 10000 per hour.
12. The method of any of claims 1 and 2, wherein the first purge gas stream and the second purge gas stream comprise H₂, CO, CO₂, CH₄, or combinations thereof.
13. The method of any of claims 1 and 2, further comprising:
recycling the first recycle stream to the first methanol synthesis reactor, wherein the first recycle stream comprises unreacted hydrogen, unreacted carbon monoxide, and unreacted carbon dioxide.
14. The method of any of claims 1 and 2, further comprising:
recycling the second recycle stream to the second methanol synthesis reactor, wherein the second recycle stream comprises unreacted hydrogen, unreacted carbon monoxide, and unreacted carbon dioxide.
15. A method of producing methanol, the method comprising:
dry-reforming natural gas to produce a first syngas stream comprising hydrogen, carbon monoxide, and/or carbon dioxide;
flowing at least some of the first syngas stream to a first methanol synthesis reactor;
separating at least some of the first syngas stream via a hydrogen/carbon monoxide separation unit to form a first hydrogen stream and a first carbon monoxide stream;
flowing the first hydrogen stream to the first methanol synthesis reactor;
reacting the carbon monoxide and/or carbon dioxide of the first syngas stream with the hydrogen of the first hydrogen stream and the hydrogen of the first syngas

stream in the first methanol synthesis reactor under reaction conditions sufficient to form methanol;

separating an effluent from the first methanol synthesis reactor to form a first methanol stream and a first byproduct stream;

splitting at least some of the first byproduct stream to form a first purge gas stream and a first recycle stream;

steam reforming natural gas to produce a second syngas stream comprising hydrogen, carbon monoxide, and carbon dioxide;

flowing the second syngas stream through a second methanol synthesis reactor;

injecting carbon dioxide and/or carbon monoxide to the second syngas stream to ensure a stoichiometric number of hydrogen to carbon monoxide (S_N) flowing into the second methanol synthesis in a range of 2 to 2.1;

reacting the hydrogen, the carbon monoxide, and the carbon dioxide in the second syngas stream in the second methanol synthesis reactor under reaction conditions sufficient to form methanol;

separating an effluent from the second methanol synthesis reactor to form a second methanol stream and a second byproduct stream;

splitting at least some of the second byproduct stream to form a second purge gas stream and a second recycle stream;

flowing at least some of a combined stream of the first purge gas stream and the second purge gas stream through a first hydrogen separation unit to form a second hydrogen stream and a first residue gas stream;

flowing the second hydrogen stream to the first syngas stream;

flowing at least some of the combined stream of the first purge gas stream and the second purge gas stream through a third methanol synthesis reactor, wherein the combined stream comprises primarily hydrogen, carbon monoxide, and/or carbon monoxide;

flowing the first carbon monoxide stream to the third methanol synthesis reactor;

injecting carbon monoxide and/or carbon dioxide to the third methanol synthesis reactor;

reacting the hydrogen in the third methanol synthesis reactor with carbon monoxide and/or carbon dioxide in the third methanol synthesis reactor under reaction conditions sufficient to form methanol and a third purge gas stream;

flowing the third purge gas stream to a second hydrogen separation unit; separate the third purge gas stream in the second hydrogen separation unit to form a third hydrogen stream and a second residue stream; and flowing the third hydrogen stream to the first syngas stream.

16. The method of claim 15, wherein the first syngas stream flowing in the first methanol synthesis reactor and the second syngas stream flowing in the second methanol synthesis reactor each has a stoichiometric number of hydrogen to carbon monoxide (S_N) equal to or greater than 2.

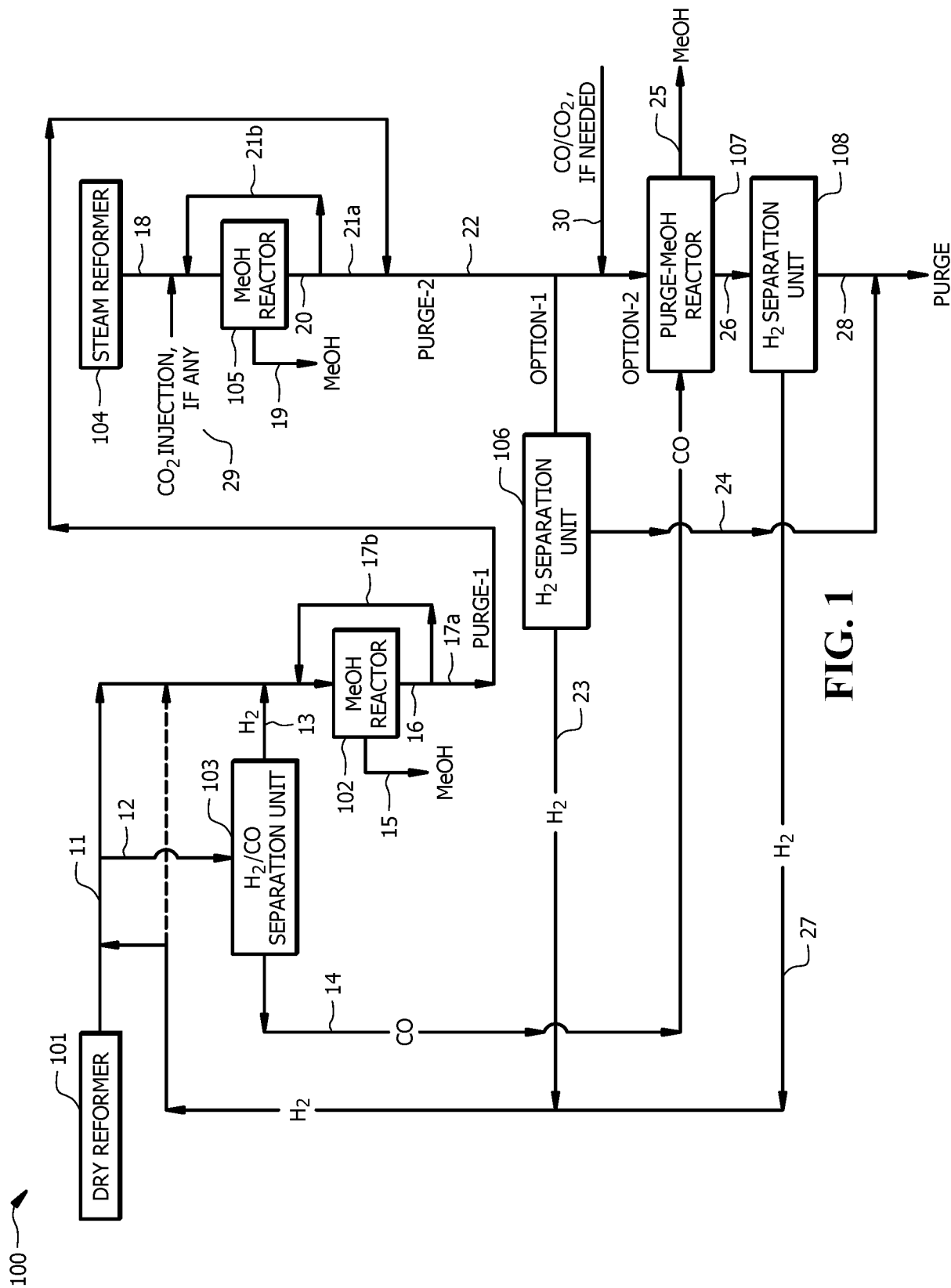


FIG. 1

200

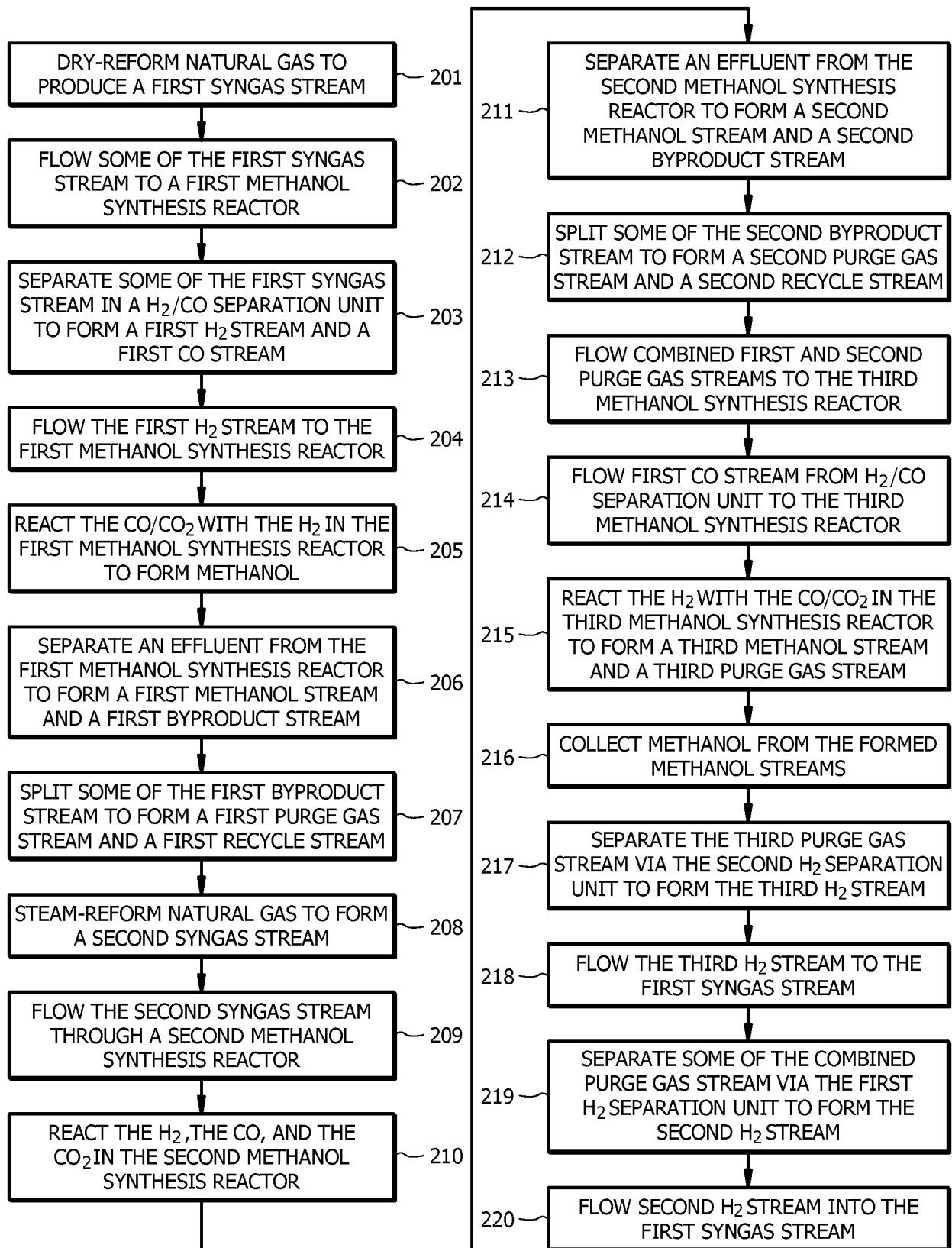


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2018/055441

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C29/15 C07C29/152 C07C31/04
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)

EP0-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2013/005840 A1 (WYNN NICOLAS P [US] ET AL) 3 January 2013 (2013-01-03) Claim 1, [004]-[0047] -----	1-16
A	US 2016/176793 A1 (CHAKRAVARTI SHRIKAR [US] ET AL) 23 June 2016 (2016-06-23) Claim 1, example -----	1-16
A	US 2008/319093 A1 (OLAH GEORGE A [US] ET AL) 25 December 2008 (2008-12-25) the whole document -----	1-16
A	WO 2016/069385 A1 (SABIC GLOBAL TECHNOLOGIES BV [NL]; MAMEDOV AGHADDIN [US]) 6 May 2016 (2016-05-06) the whole document ----- -/-	1-16



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"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

4 October 2018

Date of mailing of the international search report

23/10/2018

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2018/055441

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	LEI SHI ET AL: "An Introduction of CO₂ Conversion by Dry Reforming with Methane and New Route of Low-Temperature Methanol Synthesis", ACCOUNTS OF CHEMICAL RESEARCH., vol. 46, no. 8, 20 August 2013 (2013-08-20), pages 1838-1847, XP055401391, US ISSN: 0001-4842, DOI: 10.1021/ar300217j the whole document -----	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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