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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,
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patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the
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(54) Title: METHOD FOR THE PREPARATION OF METHANOL SYNTHESIS GAS

(57) Abstract: Method for the preparation of methanol synthesis gas combining two-step reforming and steam reforming of a carbon dioxide containing feed in parallel.5



WO 2020/148376 A1

Title: Method for the preparation of methanol synthesis gas

5 The present application is directed to the preparation of methanol synthesis gas. More particular, the invention combines two-step reforming and steam reforming in parallel.

10 Production of synthesis gas e.g. for the methanol synthesis with natural gas feed is typically carried out by steam reforming or a combination of steam reforming and oxygen reforming.

The principal reaction of steam reforming is (given for methane):



And oxygen reforming (given for methane):



Similar reactions occur for other hydrocarbons. Any reforming is normally accompanied by the water gas shift reaction:



Performing steam reforming, also known as SMR, and oxygen reforming, also known as autothermal reforming or in short ATR, in series is known as two-step reforming.

More details of steam reforming and 2-step reforming can be found in the literature.

5 The product gas from 2-step reforming comprises hydrogen, carbon monoxide, and carbon dioxide as well as other components normally including methane and steam.

10 Methanol synthesis gas has preferably a composition corresponding to a so-called module ($M = (H_2 - CO_2) / (CO + CO_2)$) of 1.90-2.20 or more preferably slightly above 2 (eg. 2.00-2.10).

15 2-step reforming produces the above mentioned preferred stoichiometric module.

It is an increasing desire in the chemical industry to reduce emission of carbon dioxide and/or to utilize carbon dioxide as feed or a part of the feed in the production of chemical products.

20 In existing or new methanol plants employing or designed with two-step reforming in the preparation of methanol synthesis gas, use of carbon dioxide as at least a part of the reforming feed is not an option because two-step reforming produces the stoichiometric correct synthesis gas for the methanol production leaving limited or no possibility for adding carbon dioxide to the reforming process.

30 We have found a method for the production of methanol synthesis gas utilizing carbon dioxide by combining two-step reforming with a steam reforming step arranged in parallel

to the two step reforming, where in the parallel steam reforming step carbon dioxide is used as part of the reforming feed.

5 Thus, this invention provides in one aspect a method for the preparation of a methanol synthesis gas comprising the steps of

(a) providing a first feed comprising hydrocarbons and steam;

10 (b) providing a second feed comprising hydrocarbons, steam and carbon dioxide;

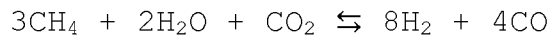
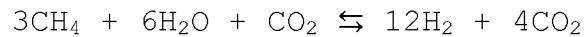
(c) reforming the first feed in a two step steam reforming process, to a first synthesis gas comprising hydrogen, carbon monoxide and carbon dioxide having a module M of
15 2.05 ± 0.2 , where M is $(H_2 - CO_2) / (CO + CO_2)$;

(d) steam reforming the second feed in parallel with the two-step reforming process) in step (c) to a second synthesis gas comprising hydrogen, carbon monoxide and carbon dioxide; and

20 (e) employing the first and second synthesis gas in combination thereof as feed for methanol synthesis.

The content of carbon dioxide in the second feed is preferably controlled to obtain a module M of 1.6 to 2.6, preferably between 1.85 to 2.35, in the second synthesis gas
25 withdrawn from the steam reforming.

As an example, for a natural gas containing only methane, a natural gas/ CO_2 ratio of 3 as feed to a steam reformer will
30 result in a synthesis gas outlet the steam reformer with $M = 2$ as shown by below two reforming equations take place for methane



5

It is further preferred that the methanol synthesis gas obtained by the method according to the invention has a module M of 1.6 to 2.6, preferably between 1.85 and 2.35.

10

In an embodiment of the invention the methanol synthesis gas is in a downstream step converted to a methanol product.

15

The steam reforming in step (d) can be performed in a conventional tubular reformer, a tubular reformer followed by an adiabatic reformer where carbon dioxide is added before and/or after the tubular reformer, a bayonet type reformer, a convective reformer or a tubular reformer where carbon dioxide is added into the reformer tubes after the feed has initially come into contact with the reforming catalyst.

20

A suitable reforming catalyst composition for use in the steam reforming depends on the amount of carbon dioxide added to the feed and the type of reformer used in the steam reforming. In most cases, a nickel catalyst is sufficient, but for high carbon dioxide contents in the feed, noble metal catalysts may be required for some types of steam reformers.

25

30

The carbon dioxide for use in the method according to the invention can advantageously be obtained from flue or off-

gasses, such as e.g. flue gas stemming from the burners in the steam reformers.

Depending on the feed composition it might be preferred to
5 desulfurize the first feed upstream the two-step reforming and/or the second feed upstream the steam reforming.

An advantage of the method according to the invention is
i.a. a reduced energy consumption and a reduced CO₂ foot-
10 print.

As already mentioned hereinbefore, the invention is addi-
tional useful in increasing production capacity of existing
methanol plants based on two step reforming in the produc-
15 tion of methanol synthesis gas or other methanol plants where the reforming section generates a synthesis gas close to stoichiometric M about 2.

Accordingly, a further aspect of the invention is a method
20 for revamping methanol synthesis gas plant, comprising adding a steam reformer in parallel to an existing two-step reforming section;
connecting the steam reforming section to a carbon dioxide source; and
25 connecting an outlet line of the parallel steam reforming section to an outlet line of the existing two-step reforming section or connecting the outlet line of the parallel steam reforming section to an existing methanol reactor in the methanol synthesis plant.

Claims

1. A method for the preparation of a methanol synthesis
5 gas comprising the steps of
(a) providing a first feed comprising hydrocarbon and
steam;
(b) providing a second feed comprising hydrocarbon, steam
and carbon dioxide, where the molecular CO_2 /hydrocarbon ra-
10 tio is between 0.1 and 0.6, preferably between 0.25 and 0.4
(c) reforming the first feed in a two step steam reforming
process to a first synthesis gas comprising hydrogen, car-
bon monoxide and carbon dioxide and having a module M of
2.05 +/- 0.2, where M is $(\text{H}_2 - \text{CO}_2) / (\text{CO} + \text{CO}_2)$;
15 (d) steam reforming the second feed in parallel with the
two-step reforming process in step (c) to a second synthesis
gas comprising hydrogen, carbon monoxide and carbon diox-
ide; and
(e) employing the first and second synthesis gas in combi-
20 nation thereof as feed for methanol synthesis.
2. The method of claim 1, comprising the further step of
desulfurizing the first feed upstream the two step steam
reforming process.
25
3. The method of claim 1 or 2, comprising the further
step of desulfurizing the second feed upstream the tubular
steam reforming.
- 30 4. The method of any one of claims 1 to 3, wherein the
second synthesis gas has a module M of 1.6 to 2.6, prefera-
bly between 1.85 to 2.35.

5. The method of any one of claims 1 to 4, wherein the methanol synthesis gas has a module M of 1.9 to 2.2.

5 6. The method of any one of claim 1 to 4, wherein the carbon dioxide in the second feed is obtained from flue and/or off-gas and/or imported to plant.

7. The method of any one of claims 1 to 6, wherein the
10 steam reforming in step (d) is performed in a standard tubular reformer, a tubular reformer followed by an adiabatic reformer where carbon dioxide is added before and/or after the tubular reformer, a bayonet type reformer, a convective reformer or a tubular reformer where carbon dioxide is
15 added into the reformer tubes after the feed has initially come into contact with the reforming catalyst.

8. The method of any one of claims 1 to 7, wherein the methanol synthesis gas is in a further step converted to a
20 methanol product.

9. A method for revamping methanol synthesis gas plant, comprising
adding a steam reformer in parallel to an existing two-step
25 reforming section;
connecting the steam reforming section to a carbon dioxide source; and
connecting an outlet line of the parallel steam reforming
section to an outlet line of the existing two-step reform-
30 ing section or connecting the outlet line of the parallel steam reforming section to an existing methanol reactor in the methanol synthesis plant.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B3/38 C07C29/151 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 C01B

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.
Y	US 2016/176793 A1 (CHAKRAVARTI SHRIKAR [US] ET AL) 23 June 2016 (2016-06-23) claims; examples figures paragraph [0037]	1-9
Y	ROSTRUP-NIELSEN J R: "PRODUCTION OF SYNTHESIS GAS", CATALYSIS TODAY, AMSTERDAM, NL, vol. 18, 1 January 1993 (1993-01-01), pages 305-324, XP000949197, DOI: 10.1016/0920-5861(93)80059-A page 314, paragraph 2 - page 315, paragraph 1 page 314; figures 6,7 ----- -/-	1-9



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2016/178915 A1 (VELOCYS TECH LTD [GB]; STEYNBERG ANDRE [US]) 10 November 2016 (2016-11-10) claims; figures -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

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