

(19)



(11)

EP 4 114 793 B9

(12)

CORRECTED EUROPEAN PATENT SPECIFICATION

(15) Correction information:

Corrected version no 1 (W1 B1)
Corrections, see
Claims EN 4

(51) International Patent Classification (IPC):

C01B 3/48 ^(2006.01) **B01D 3/00** ^(2006.01)
B01D 3/38 ^(2006.01) **C01B 3/50** ^(2006.01)

(48) Corrigendum issued on:

07.08.2024 Bulletin 2024/32

(52) Cooperative Patent Classification (CPC):

C01B 3/48; B01D 19/0015; C01B 3/50;
C01B 2203/0205; C01B 2203/0283; C01B 2203/04;
C01B 2203/048; C01B 2203/0495; C01B 2203/148;
Y02P 20/52

(45) Date of publication and mention of the grant of the patent:

01.05.2024 Bulletin 2024/18

(86) International application number:

PCT/EP2021/055050

(21) Application number: **21709384.8**

(87) International publication number:

WO 2021/175784 (10.09.2021 Gazette 2021/36)

(22) Date of filing: **01.03.2021**

(54) **PROCESS FOR THE PRODUCTION OF SYNTHESIS GAS**

VERFAHREN ZUR HERSTELLUNG VON SYNTHESSEGAS

PROCÉDÉ DE PRODUCTION DE GAZ DE SYNTHÈSE

(84) Designated Contracting States:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR

(72) Inventor: **DAHL, Per Juul**

2950 Vedbæk (DK)

(30) Priority: **03.03.2020 DK PA202000270**

(74) Representative: **Topsoe A/S**

Haldor Topsøes Allé 1
2800 Kgs. Lyngby (DK)

(43) Date of publication of application:

11.01.2023 Bulletin 2023/02

(56) References cited:

WO-A1-2018/162594 US-A- 4 681 603
US-A1- 2012 273 355 US-A1- 2015 315 020

(73) Proprietor: **Topsoe A/S**
2800 Kgs. Lyngby (DK)

EP 4 114 793 B9

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] The present invention relates to a process for the production of synthesis gas.

[0002] WO 2018/162594 A1 discloses a process comprising reforming a hydrocarbon feed gas in a reforming section obtaining a synthesis gas comprising CH₄, CO, CO₂, H₂ and H₂O and shifting the synthesis gas in a shift section comprising one or more shift steps preferably in series and optionally washing the synthesis gas leaving the shift section with water. A process condensate originating from cooling and washing the synthesis gas leaving the shift and/or the washing section is sent to a process condensate stripper, wherein dissolved shift by-products and dissolved gases are stripped out of the process condensate using steam, resulting in a stripper steam stream and using at least part of it as the H₂O added upstream the shift section and/or between the shift steps in the shift section.

[0003] Synthesis gas is typically produced by reforming a hydrocarbon feed stock either by steam reforming (SMR), secondary reforming, such as autothermal reforming (ATR) and two-step reforming with SMR and ATR in series.

[0004] The synthesis gas leaving the reforming process contains hydrogen, carbon monoxide and carbon dioxide together with unconverted hydrocarbons, usually methane.

[0005] The synthesis gas contains additionally small amounts of nitrogen stemming from the hydrocarbon feed or from the air employed in the secondary or autothermal reformer. The nitrogen will cause formation of ammonia in the reforming section corresponding to the conditions in the last reforming step. The ammonia formation is an equilibrium reaction

[0006] In number of process applications, carbon monoxide and carbon dioxide contained in the synthesis gas from the reforming process must be removed prior to synthesis gas is introduced into the process. This is in particular true in the preparation of ammonia and hydrogen.

[0007] For this purpose, carbon monoxide is converted to carbon dioxide, which can be removed by known chemical or physical carbon dioxide processes.

[0008] Carbon monoxide is converted to carbon dioxide by passing the synthesis gas through a shift section where carbon monoxide is converted to carbon dioxide by the water gas shift process.

[0009] It is well known that a shift reaction cannot be performed without formation of by-products. Most Shift catalysts contain Cu. For these catalysts, one important by-product formed in the shift reaction is methanol. Methanol reacts to amines with ammonia formed in the reforming process from the nitrogen being present in the hydrocarbon feed and/or in air as mentioned hereinbefore.

[0010] The shifted synthesis gas is subsequent to the shift section cooled and passed into a condenser where process condensate is separated from the shifted synthesis gas.

[0011] The ammonia and amines contained in the shifted synthesis gas are condensed out together with the process condensate after the shift section.

[0012] Typically, the process condensate is sent to a medium pressure (MP) steam stripper where dissolved gases inclusive ammonia and amines are stripped off with steam in order to allow the stripped condensate to be passed to boiler feed water (BFW) water treatment.

[0013] The medium pressure is defined as a pressure which is 0.5 bar, preferably 1 bar, higher than the pressure inlet the reforming section

[0014] The steam exiting the steam stripper contains the dissolved gases and the ammonia and amines by-products. This so-called stripper stream is employed as part of or all the feed steam to the reforming section and as part of or all optional steam admitted to the process downstream the reforming section upstream the last shift reactor.

[0015] The amines react in the reforming section to N₂, CO₂, CO, H₂ and H₂O.

[0016] The ammonia and amines added downstream the reforming section upstream the last shift reactor will accumulate in the section and thus cause increased level of ammonia and amines in the process condensate. Newly formed ammonia is continuously admitted to the shift section from the reforming section. The formed amines and the residual ammonia will only be removed by stripper steam admitted to the reforming section.

[0017] A problem arises when the content of amines is high in the feed steam to the reforming section as this leads to carbon formation in the reforming section either in the preheat equipment or on the catalyst bed.

[0018] The invention solves this problem by purging the required part of the process condensate prior to the MP stripper thus reducing the amine level at inlet of the reforming section to an acceptable level.

[0019] The purge can be handled in a separate unit, for example a low pressure stripper from where the dissolved gases, ammonia and amines can be released as off-gas and can be used as fuel.

[0020] The low pressure is defined as a pressure which is lower than the pressure inlet the reforming section, for example 0.5 bar g to 20. bar g or 1.5 bar g to 10 bar g or preferably 2.0 bar g to 7. bar g

[0021] In a further embodiment all stripper steam can be admitted downstream the reforming section upstream the last shift reactor. The built-up of ammonia and amines in the shift section will in this case be control by the rate of process condensate purge flow.

[0022] Thus, the invention is a process for producing synthesis gas, the A process for producing synthesis gas, the process comprising the steps of

EP 4 114 793 B9

a) reforming a hydrocarbon feed in a reforming section thereby obtaining a synthesis gas comprising CH₄, CO, CO₂, H₂ and H₂O and impurities comprising ammonia;

b) shifting the synthesis gas in a shift section comprising one or more shift steps in series to a shifted synthesis gas;

c) separating from the shifted synthesis gas a process condensate originating from cooling and optionally washing of the shifted synthesis gas;

d) passing a part of the process condensate to a condensate steam stripper, wherein dissolved shift byproducts comprising ammonia, methanol and amines formed during shifting the synthesis gas are stripped out of the process condensate using steam resulting in a stripper steam stream,

e) adding the stripper steam stream from the process condensate steam stripper to the hydrocarbon feed and/or to the synthesis gas downstream the reforming section, upstream the last shift step, wherein the remaining part of the process condensate is purged.

[0023] In an embodiment of the invention, the remaining part of the process condensate is passed via a purge line to a purge condensate steam stripper.

[0024] The amount of purged condensate can be set to reject all or part of the amines from the stripper stream added to the hydrocarbon feed and/or to the synthesis gas in step (e). In case of partly rejection, remaining amines can be removed by admitting an acceptable level of amines to the reforming section via the condensate steam stripper.

[0025] In an embodiment of the invention, the condensate steam stripper is typically an MP stripper, as mentioned hereinbefore.

[0026] In further an embodiment, the purge condensate steam stripper is a low pressure stripper.

[0027] The stripper steam from purge condensate steam stripper is condensed and the resulting non-condensable gases containing amines, are advantageously employed as fuel for example in the reforming section and the liquid condensate is returned to the top of the low pressure stripper.

[0028] Thus, in an embodiment, steam from the purge gas steam stripper is condensed and non-condensable gases are employed as fuel.

[0029] The stripped condensate and the stripped purge condensate leave the bottom of the condensate steam stripper and purge condensate steam stripper and is send to water treatment.

[0030] The amount of the purge condensate is adjusted to remove all or part of the amines and ammonia formed in the reforming and shift section. In case of partly removal, remaining amines and ammonia can be removed by admitting an acceptable level of amines and ammonia to the reforming section via the stripper steam from the condensate steam stripper.

Example

Reference is made to Fig. 1

[0031] The stream numbers in the tables below refers to the reference numbers in Fig.1 Table 1 shows a case for removing formed ammonia and amines by converting these in the reforming section by adding 8.4% of the stripped steam to this unit.

[0032] Table 2 shows a case for removing formed ammonia and amines by purging 8% of the process condensate.

[0033] There is in both cases the same built-up of ammonia and amines in the shift section. This built-up can be reduced or removed by admitting all the stripped steam to either the reforming section or the process condensate purge.

Table 1

Stream	1	2	3	4	5	6	7	8	9	10	11
Flow T/h	92	100	168	255	255	125	0	125	95	87	8
Ammonia Kg/g	0	40	42	482	480	480	0	480	480	440	40
Amines Kg/h	0	3	0	33	36	36	0	36	36	33	3

Table 2

Stream	1	2	3	4	5	6	7	8	9	10	11
Flow T/h	100	100	168	255	255	125	10	115	87	87	0
Ammonia Kg/g	0	0	42	480	478	478	40	438	438	438	0
Amines Kg/h	0	0	0	33	36	36	3	33	33	33	0

Claims

1. A process for producing synthesis gas, the process comprising the steps of

a) reforming a hydrocarbon feed in a reforming section thereby obtaining a synthesis gas comprising CH₄, CO, CO₂, H₂ and H₂O and impurities comprising ammonia;

b) shifting the synthesis gas in a shift section comprising one or more shift steps in series to a shifted synthesis gas;

c) separating from the shifted synthesis gas a process condensate originating from cooling and optionally washing of the shifted synthesis gas;

d) passing a part of the process condensate to a condensate steam stripper, wherein dissolved shift byproducts comprising ammonia, methanol and amines formed during shifting the synthesis gas are stripped out of the process condensate using steam resulting in a stripper steam stream,

e) adding the stripper steam stream from the process condensate steam stripper to the hydrocarbon feed and/or to the synthesis gas downstream the reforming section, upstream the last shift step, wherein

the remaining part of the process condensate is purged.

2. Process of claim 1, wherein the condensate steam stripper is a medium pressure stripper.

3. Process of claim 1 or 2, wherein the purge is passed to a purge condensate steam stripper.

4. Process of claim 3, wherein the purge condensate steam stripper is a low pressure stripper

5. Process of any one of claims 3 or 4, wherein steam from the purge condensate steam stripper is condensed and non-condensable gases are employed as fuel.

6. Process of any one of claims 1 to 5, wherein stripped condensate from step (d) is passed to water treatment.

7. Process of any one of claims 3 to 6, wherein the stripped purge condensate from the purge condensate steam stripper is passed to water treatment.

Patentansprüche

1. Prozess zur Herstellung von Synthesegas, wobei der Prozess die Schritte umfasst zum

a) Reformieren einer Kohlenwasserstoffzuführung in einem Reformierungsabschnitt, wodurch ein Synthesegas erhalten wird, das CH₄, CO, CO₂, H₂ und H₂O und Verunreinigungen umfasst, die Ammoniak umfassen;

b) Umwandeln des Synthesegases in einem Umwandlungsabschnitt, der einen oder mehrere Umwandlungsschritte in Reihe umfasst, zu einem umgewandelten Synthesegas;

c) Abscheiden eines Prozesskondensats, das aus dem Kühlen und optional Waschen des umgewandelten Synthesegases stammt, von dem umgewandelten Synthesegas;

d) Zuführen eines Teils des Prozesskondensats zu einem Kondensat-Dampfstripper, wobei gelöste Umwandlungsnebenprodukte, die Ammoniak, Methanol und Amine umfassen, welche beim Umwandeln des Synthesegases gebildet werden, unter Verwendung von Dampf aus dem Prozesskondensat gestrippt werden, woraus sich ein Stripper-Dampfstrom ergibt,

e) Zufügen des Stripper-Dampfstroms aus dem Prozesskondensat-Dampfstripper zur Kohlenwasserstoffzuführung und/oder zum Synthesegas stromabwärts des Reformierungsabschnitts, stromaufwärts des letzten Umwandlungsschritts, wobei

EP 4 114 793 B9

der restliche Teil des Prozesskondensats ausgespült wird.

2. Prozess nach Anspruch 1, wobei der Kondensat-Dampfstripper ein Mitteldruckstripper ist.
- 5 3. Prozess nach Anspruch 1 oder 2, wobei die Spülung einem Spülkondensat-Dampfstripper zugeführt wird.
4. Prozess nach Anspruch 3, wobei der Spülkondensat-Dampfstripper ein Niederdruckstripper ist.
- 10 5. Prozess nach einem der Ansprüche 3 oder 4, wobei Dampf aus dem Spülkondensat-Dampfstripper kondensiert wird und nicht kondensierbare Gase als Brennstoff eingesetzt werden.
6. Prozess nach einem der Ansprüche 1 bis 5, wobei gestripptes Kondensat aus Schritt (d) einer Wasserbehandlung zugeführt wird.
- 15 7. Prozess nach einem der Ansprüche 3 bis 6, wobei das gestrippte Spülkondensat aus dem Spülkondensat-Dampfstripper einer Wasserbehandlung zugeführt wird.

Revendications

- 20 1. Processus de production de gaz de synthèse, le processus comprenant les étapes de
 - a) reformage d'une charge d'hydrocarbures dans une section de reformage, permettant ainsi d'obtenir un gaz de synthèse comprenant CH₄, CO, CO₂, H₂ et H₂O et des impuretés comprenant de l'ammoniac ;
 - 25 b) conversion du gaz de synthèse dans une section de conversion comprenant une ou plusieurs étapes de conversion successives en un gaz de synthèse converti ;
 - c) séparation, du gaz de synthèse converti, d'un condensat de traitement provenant du refroidissement et facultativement du lavage du gaz de synthèse converti ;
 - 30 d) passage d'une partie du condensat de traitement vers un extracteur à la vapeur de condensat, dans lequel des sous-produits de conversion dissous comprenant de l'ammoniac, du méthanol et des amines formés pendant la conversion du gaz de synthèse sont extraits du condensat de traitement en utilisant de la vapeur, ce qui donne lieu à un flux de vapeur d'extracteur,
 - 35 e) ajout du flux de vapeur d'extracteur provenant de l'extracteur à la vapeur de condensat de traitement à la charge d'hydrocarbures et/ou au gaz de synthèse en aval de la section de reformage, en amont de la dernière étape de conversion, dans lequella partie restante du condensat du traitement est purgée.
- 40 2. Processus selon la revendication 1, dans lequel l'extracteur à la vapeur de condensat est un extracteur à moyenne pression.
3. Processus selon la revendication 1 ou 2, dans lequel la purge est envoyée vers un extracteur à la vapeur de condensat de purge.
- 45 4. Processus selon la revendication 3, dans lequel l'extracteur à la vapeur de condensat de purge est un extracteur à basse pression.
5. Processus selon l'une quelconque des revendications 3 ou 4, dans lequel la vapeur provenant de l'extracteur à la vapeur de condensat de purge est condensée et des gaz non condensables sont employés comme combustible.
- 50 6. Processus selon l'une quelconque des revendications 1 à 5, dans lequel le condensat extrait de l'étape (d) est envoyé au traitement de l'eau.
- 55 7. Processus selon l'une quelconque des revendications 3 à 6, dans lequel le condensat de purge extrait provenant de l'extracteur à la vapeur de condensat de purge est envoyé au traitement de l'eau.

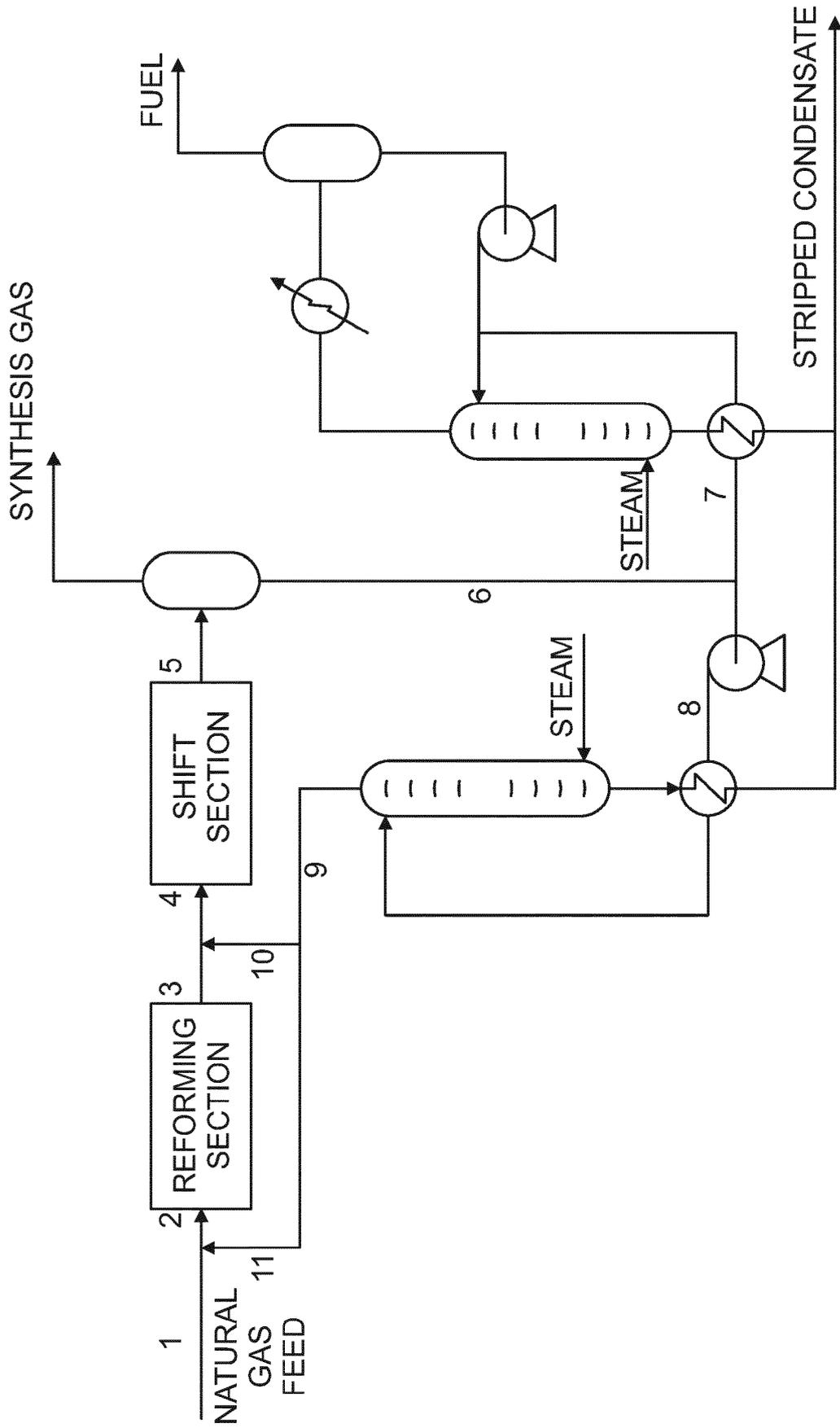


Fig. 1

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 2018162594 A1 [0002]