(12) STANDARD PATENT (11) Application No. AU 2018305811 B2
(19) AUSTRALIAN PATENT OFFICE

(54) Title
Method for improving efficiency of an ammonia synthesis gas plant

(51) International Patent Classification(s)
C01B 3/02 (2006.01) ***C01B 13/02*** (2006.01)
C01B 3/38 (2006.01) ***C01C 1/04*** (2006.01)
C01B 3/48 (2006.01) ***C25B 1/04*** (2006.01)
C01B 3/58 (2006.01)

(21) Application No: **2018305811** (22) Date of Filing: **2018.07.11**

(87) WIPO No: **WO19/020377**

(30) Priority Data

(31) Number	(32) Date	(33) Country
PA 2017 00425	**2017.07.25**	**DK**
PA 2017 00522	**2017.09.25**	**DK**

(43) Publication Date: **2019.01.31**
(44) Accepted Journal Date: **2023.11.23**

(71) Applicant(s)
Haldor Topsøe A/S

(72) Inventor(s)
HAN, Pat A.;KRØLL JENSEN, Annette E.

(74) Agent / Attorney
Griffith Hack, Level 10 161 Collins St, MELBOURNE, VIC, 3000, AU

(56) Related Art
WO 2016/149507 A1
JP 2011132103 A
US 2012/0100062 A1
CN 101892492 A
US 4681745 A
US 2016/0369411 A1

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
31 January 2019 (31.01.2019)

WIPO | PCT

(10) International Publication Number
WO 2019/020377 A1

(51) International Patent Classification:
C01B 3/02 (2006.01) *C25B 1/04* (2006.01)
C01B 3/38 (2006.01) *C01B 3/48* (2006.01)
C01C 1/04 (2006.01) *C01B 3/58* (2006.01)
C01B 13/02 (2006.01)

(21) International Application Number:
PCT/EP2018/068806

(22) International Filing Date:
11 July 2018 (11.07.2018)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PA 2017 00425 25 July 2017 (25.07.2017) DK
PA 2017 00522 25 September 2017 (25.09.2017) DK

(71) Applicant: HALDOR TOPSØE A/S [DK/DK]; Haldor Topsøes Allé 1, 2800 Kgs. Lyngby (DK).

(72) Inventors: HAN, Pat A.; Krokushaven 15, 2765 Smørum (DK). KRØLL JENSEN, Annette E.; Maglegårdsvej 327, 3480 Fredensborg (DK).

(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, 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 the identity of the inventor (Rule 4.17(i))*
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*
— *of inventorship (Rule 4.17(iv))*

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

(54) Title: METHOD FOR IMPROVING EFFICIENCY OF AN AMMONIA SYNTHESIS GAS PLANT

(57) Abstract: Method for improving efficiency of an existing ammonia synthesis gas plant or a new ammonia synthesis gas plant by establishing a combination of secondary steam reforming using oxygen from electrolysis of water for the production of ammonia synthesis gas.

WO 2019/020377 A1

Title: Method for improving efficiency of an ammonia synthesis gas plant

The present application is directed to the preparation of ammonia synthesis gas. More particular, the invention is a method for improving efficiency of a conventional ammonia synthesis gas plant by combining electrolysis of water and the conventional primary and secondary steam reforming of a hydrocarbon feed stock for the preparation of hydrogen and nitrogen containing ammonia synthesis gas.

Ammonia synthesis gas is conventionally prepared by subjecting hydrocarbon feed typically natural gas and/or higher hydrocarbons to endothermic steam reforming reactions in a fired tubular primary steam reformer by contact with a steam reforming catalyst. The primary reformed gas is then fed into a secondary adiabatic steam reformer, wherein part of hydrogen formed in the primary steam reforming and residual amounts of hydrocarbons in the gas from the primary steam reforming are partial oxidized with air and steam and subsequently reformed in presence of a secondary reforming catalyst. From the secondary reformer, raw synthesis gas is withdrawn containing hydrogen, carbon monoxide and carbon dioxide formed during reaction of the feedstock in the above steam reforming reactions and nitrogen introduced into the gas through addition of air in the secondary reforming step.

The disadvantage of the primary and secondary reforming process is a relatively high hydrocarbon feed stock and fuel consumption for use in heating the endothermic primary steam reforming in the fired primary steam reformer and consequently a large CO_2 emission in the flue gas from burners used to heat the reformer. The CO_2 product can be captured from the process and used for downstream processes such as urea production or enhanced oil recovery.

However, primary and secondary steam reforming is still frequently employed in the industry, particularly in existing reforming plants for the production of ammonia synthesis gas.

Secondary steam reforming comprises partial oxidation, using oxygen containing atmosphere, of a primary reformed feed gas to CO, CO_2, H_2, H_2O and remaining hydrocarbon and subsequently steam reforming of the hydrocarbon to form raw synthesis gas.

Recently, a combination of electrolysis of water for production of hydrogen and air separation for the production of nitrogen has been envisaged for the preparation of ammonia synthesis gas, at least in patent literature. The thus produced hydrogen and nitrogen are combined in stoichiometric ratios to form synthesis gas for ammonia production. The disadvantage of the combination of electrolysis and air separation is, however, that oxygen is produced as by-product in both electrolysis and air separation, which has no use in the ammonia synthesis, and can be considered as energy loss.

Typically, existing industrial ammonia synthesis gas plants, the so-called front end of an ammonia plant comprise as already mentioned above, a fired primary steam reformer, a secondary steam reformer with a burner at gas inlet side and a steam reforming catalyst bed at gas outlet side. The burner is typically operated with air.

The raw ammonia synthesis gas withdrawn from the secondary steam reformer is subsequently treated in a water gas shift unit for the production of further hydrogen and conversion of carbon monoxide to carbon dioxide by the known water gas shift reaction.

The carbon dioxide contained in the shifted ammonia synthesis gas is then removed in a carbon dioxide removal process.

Remaining amounts of carbon dioxide and/or carbon monoxide in the ammonia synthesis gas from the carbon dioxide removal process are removed by methanation in a chemical reaction that converts carbon monoxide and/or carbon dioxide to methane.

The thus prepared ammonia synthesis gas is introduced into an ammonia make up gas compressor and sent into the ammonia production unit.

The present invention is based on establishing a combination of the fired primary steam reforming process and the secondary reforming process using air or oxygen enriched air in the operation of the secondary reformer burner and a new implemented step of electrolysis of water for the production of ammonia synthesis gas.

Thus, in a first aspect of the present invention there is provided a method of improving efficiency of an ammonia synthesis gas plant, wherein the ammonia synthesis gas plant comprises a fired primary steam reformer and a secondary steam reformer operated with an oxygen containing atmosphere, a water gas shift unit, a carbon dioxide removal unit, a methanation step and an ammonia synthesis gas compressor, the method comprising

(a) establishing an electrolysis unit and preparing a separate hydrogen gas containing stream and a separate oxygen gas containing stream by electrolysis of water;

(b) establishing a gas pipe for transporting the separate hydrogen gas containing stream from the electrolysis unit to the synthesis gas compressor and/or to the methanation step; and

(c) establishing a gas pipe for transporting at least part of the separate oxygen gas stream from the electrolysis unit to a burner in the secondary reformer.

In another aspect of the present invention there is provided an Improved ammonia synthesis gas plant comprising a fired primary steam reformer and a secondary steam reformer operated with an oxygen containing atmosphere, a water gas shift unit, a carbon dioxide removal unit, a methanation reactor and an ammonia synthesis gas compressor, wherein the ammonia synthesis gas plant further comprises an electrolysis unit providing a separate hydrogen containing stream and a separate oxygen gas containing stream by elec trolysis of water and a gas pipe for transporting the separate hydrogen gas containing stream from the electrolysis unit to the synthesis gas compressor and/or to the methanation reactor and a gas pipe for transporting at least part of the separate oxygen gas stream from the electrolysis unit upstream or into a burner in the secondary reformer.

The method of the invention can be used to improve efficiency of an existing ammonia synthesis gas plant operated with primary and secondary reforming or in a new plant with primary and secondary reforming. The improvement of an existing or a new ammonia synthesis gas plant by the method of the invention aims to increase the production capacity of the plant and/or to save fuel in the fired primary steam reformer at a fixed capacity, as oxygen from water electrolysis provides heat for the reforming reaction in the secondary reformer. Thereby, the duty of the primary reformer is decreased, when the oxygen content in the oxygen containing atmosphere in the secondary reformer is increased with the oxygen prepared in the water electrolysis. As a result, the hydrocarbon slip in the gas from the primary reformer increases and the gas exit temperature decreases, which again results in lower fuel consumption for firing the primary reformer. Due to the lower fuel consumption, the reformer tube wall temperature is reduced, resulting in a significantly longer tube life time.

Another advantage is that the overall hydrocarbon slip outlet the secondary reformer can be the same as in conventional plants without electrolysis or can be reduced to obtain improved synthesis gas composition because of reduced content of inerts resulting in reduced purge from the ammonia loop and thus a more efficient utilization of the feed stock.

The method according to the invention provides further advantage of less emission of CO_2 from the primary flue gas stack.

Still an advantage is that the CO_2 partial pressure is increased at inlet to the carbon dioxide removal unit, which improves the carbon dioxide removal efficiency by reducing the required energy consumption.

Compared to prior art methods using electrolysis of water for hydrogen production and air separation for nitrogen production, the oxygen product from electrolysis of water is advantageously used for partial oxidation in secondary reformer resulting in a reduced size of the primary reformer in a new plant or reduced load in an existing plant, which is a costly and an energy intensive unit and process.

Still an advantage of the invention is that energy for operating the electrolysis unit can be renewable energy generated by windmills, solar cells, hydraulic energy or other renewables.

Thus, in a preferred embodiment of the invention, the electrolysis unit is powered by renewable energy.

Preferably, the electrolysis of water is performed at elevated pressure according to process air compressor discharge pressure, which delivers the prepared stream of oxygen at elevated pressure to the burner of the secondary reformer and the hydrogen stream to the synthesis gas compressor and/or to the methanation step.

Thus, in a preferred embodiment of the invention, the electrolysis unit is pressurized.

The synergy in combining water electrolysis with secondary reforming technology for ammonia synthesis gas production, results in overall savings of hydrocarbon feedstock and fuel for the reforming process.

It is to be understood that, if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

In Table 1 below, key figures of ammonia synthesis gas preparation are given for a 2200 MTPD ammonia plant for comparison of conventional syngas technologies and conventional syngas technology combined with water electrolysis.

Technology for syngas preparation	Natural gas feed consumption, Nm^3/h	Natural gas fuel consumption, Nm^3/h	Power for electrolysis, MW	CO_2 in flue gas, Nm^3/h	Primary reformer duty, Gcal/h	T_{out} Primary Reformer, °C
Conventional	57,408	19,273	0	21,899	108.82	807
Conventional with water electrolysis (25% oxygen in air)	57,108	14,072	54	16,438	82.34	748

Table 1

Claims

1. A method of improving efficiency of an ammonia synthesis gas plant, wherein the ammonia synthesis gas plant comprises a fired primary steam reformer and a secondary steam reformer operated with an oxygen containing atmosphere, a water gas shift unit, a carbon dioxide removal unit, a methanation step and an ammonia synthesis gas compressor, the method comprising

(a) establishing an electrolysis unit and preparing a separate hydrogen gas containing stream and a separate oxygen gas containing stream by electrolysis of water;

(b) establishing a gas pipe for transporting the separate hydrogen gas containing stream from the electrolysis unit to the synthesis gas compressor and/or to the methanation step; and

(c) establishing a gas pipe for transporting at least part of the separate oxygen gas stream from the electrolysis unit to a burner in the secondary reformer.

2. The method according to claim 1, wherein the electrolysis unit is powered by renewable energy.

3. The method according to claim 1 or 2, wherein the oxygen containing atmosphere is air enriched with oxygen from the separate oxygen gas stream.

4. The method according to any one of claims 1 to 3, wherein the electrolysis unit is pressurized.

5. Improved ammonia synthesis gas plant comprising a fired primary steam reformer and a secondary steam reformer operated with an oxygen containing atmosphere, a water gas shift unit, a carbon dioxide removal unit, a methanation reactor and an ammonia synthesis gas compressor, wherein the ammonia synthesis gas plant further comprises an electrolysis unit providing a separate hydrogen containing stream and a separate oxygen gas containing stream by electrolysis of water and a gas pipe for transporting the separate hydrogen gas containing stream from the electrolysis unit to the synthesis gas compressor and/or to the methanation reactor and a gas pipe for transporting at least part of the separate oxygen gas stream from the electrolysis unit upstream or into a burner in the secondary reformer.