(19) DANMARK

(10) **DK/EP 4288383 T3**

(12) Oversættelse af europæisk patentskrift

Patent- og Varemærkestyrelsen

(51) Int.Cl.: ***C 01 B 3/32 (2006.01)*** ***C 01 B 3/12 (2006.01)*** ***C 01 B 3/38 (2006.01)*** ***C 01 B 3/48 (2006.01)*** ***C 01 B 3/50 (2006.01)*** ***C 01 B 3/56 (2006.01)*** ***C 07 C 29/151 (2006.01)***

(45) Oversættelsen bekendtgjort den: **2024-11-04**

(80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2024-09-11**

(86) Europæisk ansøgning nr.: **22702671.3**

(86) Europæisk indleveringsdag: **2022-01-26**

(87) Den europæiske ansøgnings publiceringsdag: **2023-12-13**

(86) International ansøgning nr.: **EP2022051764**

(87) Internationalt publikationsnr.: **WO2022167288**

(30) Prioritet: **2021-02-04 EP 21155137**

(84) Designerede stater: **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**

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(54) Benævnelse: **PROCESS AND PLANT FOR METHANOL PRODUCTION**

(56) Fremdragne publikationer:
**GB-A- 2 585 477**
**US-A1- 2018 258 019**
**US-B2- 6 706 770**

# DESCRIPTION

Description

**Field of application**

**[0001]** The present invention relates to a process and plant for the synthesis of methanol.

**Prior art**

**[0002]** The industrial preparation of methanol includes syngas preparation, methanol synthesis and methanol purification.

**[0003]** Syngas is prepared in a front-end section by subjecting a suitable hydrocarbon feedstock to a reforming process including a partial oxidation to yield a gaseous mixture of carbon oxides and hydrogen. Such mixture is commonly termed syngas or make-up gas.

**[0004]** The syngas after cooling and compression to methanol synthesis conditions is fed to a methanol synthesis loop wherein crude methanol is synthesised in a gas-solid catalytic reactor over a copper-based catalysts $CuO/ZnO/Al_2O_3$. Typical operating temperature and pressure of the synthesis reactor are 250 °C to 300 °C and 50 to 100 bar.

**[0005]** A methanol synthesis loop produces typically a stream of raw methanol and a purge gas removed from the loop. The purge gas contains unreacted hydrogen and inert compounds such as methane, argon and nitrogen. It is known to recover unreacted hydrogen from the purge gas, e.g. by means of a hydrogen recovery unit (HRU). The HRU typically operate by membrane separation or pressure swing adsorption (PSA).

**[0006]** The composition of the syngas feed to the methanol reactor is characterised by the following stoichiometric number:

$$R = (H_2 - CO_2) / (CO + CO_2).$$

**[0007]** A stoichiometric number at about 2.02 to 2.1 is generally considered optimal for most of the catalysts used in the methanol synthesis.

**[0008]** Based on the technology adopted, the syngas produced in the front-end may have a sub-stoichiometric content of hydrogen. This term denotes that the make-up gas contains less hydrogen than a target stoichiometric amount for methanol synthesis. In most cases for example a syngas stream having a stoichiometric number R lower than 2 is considered sub-stoichiometric.

**[0009]** Typically, a make-up gas with such deficiency of hydrogen is produced from stand-alone autothermal reforming fired with oxygen or oxygen-enriched air and running at a relatively low steam to carbon ratio. This technique of producing the make-up gas is interesting for its low consumption of fuel, however the drawback of the hydrogen deficit must be resolved.

**[0010]** A lack of hydrogen may result in a low efficiency and high generation of undesirable by-products such as higher alcohols and ketones. There is the need therefore to adjust the hydrogen content of the make-up gas before its introduction in the methanol reactor.

**[0011]** The hydrogen separated from the purge gas of the synthesis loop, as above described, can be used for this purpose. Unfortunately, due to the low amount of purge gas (i.e. not greater than 5%), the hydrogen that can be recovered from the loop purge may not be sufficient to reach the desired stoichiometric number in the feed.

**[0012]** Various attempts have been made in the prior art to solve this problem. US6797252 discloses a process for producing synthesis gas wherein the composition of the make-up gas is adjusted by means of a plurality of secondary reactors wherein at least one of the secondary reactors is a low-temperature water gas shift reactor and the other is a high-temperature water gas shift reactor. In the prior art, the provision of a low-temperature water gas shift reactor arranged in series after a high-temperature water gas shift reactor is deemed essential to recover the amount of hydrogen necessary to adjust the stochiometric number of the make-up gas feeds to the methanol reactor.

**[0013]** The water-gas shift reactor converts carbon monoxide and water into hydrogen and carbon dioxide. Hydrogen is separated from carbon dioxide via a $CO_2$ removal unit and is then fed to the methanol reactor to adjust the stoichiometric number.

**[0014]** This technique however requires the installation of two expensive water gas shift units; another drawback is the amount of hydrogen recovered in the WGS units is not constant during the life of the installation, due to the partial deactivation of the catalyst over time, and the stochiometric number progressively deviates from the optimum value. Currently, no methods or processes are available that allow to adjust and maintain the stoichiometric number of the syngas fed to the methanol reactor to the optimal value during the entire production cycle.

**[0015]** Additionally, conventional methanol synthesis processes are subject to an additional disadvantage when the autothermal reformer is operated at low steam to carbon molar ratio (S/C) and when a relatively high pressure is adopted e.g. S/C lower than 1.5 and pressure of about 35 to 50 bar, because under these operating conditions a relative a high content of unconverted methane is retained in the syngas.

**[0016]** Such unconverted stream is usually extracted from the methanol converter as a purge gas and after separation from hydrogen it can be recycled as fuel to fired heater. However, in case of a large amount of such waste gas to be valorised as fuel, the heating duty necessary for the process can be saturated by the waste gases alone, leading to issues of operability of the fired heater. As a result, not all of the methane-containing waste gas can be advantageously combusted. Therefore, it is desirable to find a more efficient way to exploit the methane stream. GB2585477A discloses a methanol synthesis process.

**[0017]** Therefore, in light of the drawbacks set out above, it is desirable to design a methanol process that can exploit in a more efficient way the unconverted methane stream meanwhile allowing the adjustment of the stoichiometric number of the syngas fed to the methanol reactor.

## Summary of the invention

**[0018]** The invention faces the problem of how to deal with the high content of methane retained in the purge gas stream extracted from the methanol synthesis loop. Additionally, the invention faces the problems on how to adjust the hydrogen content in the make-up gas for the synthesis of methanol, when the make-up gas is generated in a sub-stoichiometric condition. More specifically, the invention aims to provide a process wherein the synthesis loop can run efficiently when the syngas produced in the front-end has a sub-stoichiometric hydrogen content and a significant methane content.

**[0019]** Another aim is to provide a process wherein the adjustment of the hydrogen content in the feed gas can be controlled in a flexible way to conform to different operating condition, particularly to ageing and loss of efficiency of the HTS catalyst over time and variability of the feedstock used as a hydrocarbon source. A further aim is to develop a methanol plant with low capital expenditure (CAPEX) and low natural gas consumption. Still a further aim is to develop a process and plant which is scalable to a large capacity, e.g. of 10'000 tons/day of methanol, at economically attractive conditions. A further aim is to reduce emissions so that a large plant is also environmentally acceptable.

**[0020]** The above aims are reached with a process and a plant according to the claims.

**[0021]** In the process of the invention a portion of the make-up gas obtained by reforming is separated during a cooling process and before the cooling process is completed, so that it still contains a significant amount of water. This separated partially cooled make-up gas is subject to water-gas shift and hydrogen recovery, thus obtaining a first hydrogen stream. The remainder of the make-up gas is further cooled obtaining a fully cooled main stream of make-up gas.

**[0022]** A second hydrogen stream is obtained from the methanol synthesis loop purge. The first and the second hydrogen streams are added to the main stream of make-up gas to adjust its hydrogen content. The addition of the first hydrogen stream and second hydrogen stream can be performed at the same location or different locations.

**[0023]** Additionally, a methane-rich stream is also obtained from the loop purge, which is recycled as a feedstock to the reforming process for the production of make-up gas.

**[0024]** The separated portion of makeup gas is preferably a minor portion. Particularly preferably, this portion may be (in volume) not greater than 15% of the make-up gas available from the reforming process, for example 1% to 10%.

**[0025]** The invention provides a dual recovery of hydrogen by means of the shift and hydrogen purification performed on the separated portion of make-up gas, and the hydrogen recovery on the synthesis loop purge stream. This dual recovery allows more flexible control in the adjustment of the hydrogen content of the main stream of make-up gas.

**[0026]** The separated stream of fresh make-up gas represents an additional degree of freedom that can be advantageously oversized to tackle variations in the feed composition, granting good feedstock flexibility, as well as flexibility from start of run (SOR) to end of run (EOR) conditions of the HTS catalyst.

**[0027]** Particularly, an advantage of the invention is that said dual recovery of hydrogen is combined with recycle of a methane-rich stream obtained from the synthesis loop purge.

**[0028]** The shift of the separated portion of fresh make-up gas allows advantageous heat recovery, due to the elevated temperature of said stream.

**[0029]** The methane rich stream recovered from the loop purge may be obtained at a pressure level compatible with the syngas generation section, particularly when a membrane separation is adopted. Accordingly, the methane-rich stream can be recycled without recompression.

**[0030]** Preferably the first hydrogen stream is obtained with a PSA process and the second hydrogen stream is obtained with membrane separation. Obtaining the first hydrogen stream with a PSA process has further advantages. The PSA process recovers a pure hydrogen stream which is kept at the same pressure as the feed, therefore allowing mixing with the remaining part of the synthesis gas without any recompression. Additionally, the hydrogen stream produced by the PSA has a very high purity, so that a part of it can be exported for other uses, for example for ammonia co-production.

**[0031]** The reforming process may include autothermal reforming, optionally preceded by one or more pre-reforming steps.

**[0032]** The invention is particularly interesting when the makeup gas is generated by autothermal reforming. The dual hydrogen recovery and methane recovery of the invention are well suited for integration with autothermal reforming, even more when the hydrogen recovery on the synthesis loop purge is performed using a membrane based HRU, allowing the recycle without recompression of part of the methane rich retentate as feed for the autothermal reforming.

**[0033]** Still another aspect of the invention in the application is subjecting at least a portion of the make-up gas characterised by a low steam to dry gas ratio to a high-temperature water gas shift conversion step employing high-temperature water gas shift catalysts suitable to operate at low steam to dry gas ratio e.g. from 0.1 to 0.5 wherein the steam to dry gas ratio is defined as follow $S/DG=H_2O/(1-H_2O)$.

**Preferred embodiments**

**[0034]** The cooling of the makeup gas may be performed in a cooling zone comprising a plurality of heat exchangers which are arranged in series to form a cooling train so that for each pair of consecutive first and second heat exchangers of the cooling train, the effluent of a first heat exchanger is further cooled in the second heat exchanger. In such a case, a minor portion of make-up gas is separated at an intermediate point of the cooling zone before passage in at least one of the heat exchangers. Accordingly, the separated portion of makeup gas does not fully traverse the cooling train and is not completely cooled. The remainder of makeup gas is further cooled in the cooling zone to produce the fully cooled main stream of makeup gas.

**[0035]** For practical reasons, a preferred embodiment includes two heat exchanger sections in series wherein the minor portion of make-up gas is separated after a passage in the first heat exchanger section and prior to entering the second heat exchanger section. The first heat exchanger section is configured to partially cool down the make-up gas obtained from reforming. The second heat exchanger section is configured to completely cool down the remainder of make-up gas, after separation of the minor portion directed to shift and hydrogen separation.

**[0036]** The temperature of the minor portion of gas after separation is preferably 320 to 450 °C. The temperature of the second portion of gas, after complete cooling, is preferably 25 to 60 °C more preferably 45 °C.

**[0037]** Preferably, the cooling of the make-up gas is carried out by means of indirect heat transfer with water or steam. The heat exchanger sections may comprise one or more of a steam generator, a steam superheater and/or a water preheater.

**[0038]** In an embodiment, a hot water produced in the makeup gas cooling zone may be feed as a reagent to the reforming process.

**[0039]** As mentioned above, particularly preferred application of the invention concerns the generation of make-up gas by autothermal reforming, optionally after pre-reforming. Autothermal reforming is performed in a suitable autothermal reformer (ATR) in the presence of oxygen or oxygen-containing gas (air or enriched air), steam and optionally carbon dioxide over a suitable catalyst under oxidation conditions effective to produce the make-up gas. Pre-reforming, if provided, may be performed in one or more pre-reformers.

**[0040]** In a preferred embodiment, the autothermal reformer operates at low steam to carbon ratio (S/C) preferably comprised between 0.5 and 1.5, more preferably between 0.8 and 1.2. Preferably, the autothermal reformer operates at a pressure between 25 and 60 abs bar, and more preferably between 35 and 50 abs bar.

**[0041]** The water-gas shift of the separated portion of make-up gas may include catalytic high-temperature shift (HTS). A high-temperature shift may be performed at a temperature in the range 300 to 500 °C, preferably 350 to 450 °C. Preferably the water-gas shift of the separated portion is performed solely in a high-temperature shift reactor without a subsequent medium-temperature or low-temperature shift.

**[0042]** The first hydrogen recovering section includes preferably a Pressure Swing Adsorption (PSA) unit. The second hydrogen recovery section includes preferably a membrane-based hydrogen purification unit.

**[0043]** In an interesting embodiment, part of the hydrogen recovered from the PSA may be used as a fuel to meet the energy demand of the process, and/or as feedstock for the coproduction of ammonia and/or employed for other processes outside the synthesis of ammonia. The use of hydrogen from PSA as a fuel may further reduce the carbon emission of the process.

**[0044]** More specifically, the use of hydrogen recovered from the PSA ("PSA hydrogen") as a fuel gives the following advantages: the purified hydrogen obtained from the PSA can fuel the fired heaters of the plant, instead of the light hydrocarbons that are usually employed both as feedstock and fuel. The direct emissions of the plant can be reduced significantly, or eliminated completely by foreseeing a carbon capture step. The carbon to be captured remains in concentrated form in process streams at high pressure, instead of being diluted in low-pressure flue gases, making the carbon capture step less expensive.

**[0045]** The use of PSA hydrogen for ammonia co-production is also possible thanks to the high purity of hydrogen that can be produced by PSA. The highly pure PSA hydrogen stream is well suited for direct use in an ammonia synthesis loop where the specification on the hydrogen purity is very strict due to poisoning issues of the ammonia synthesis catalyst.

**[0046]** The ability to recover hydrogen from two independent sources, namely a portion of make-up gas and the loop purge, allows high flexibility in the selection of the hydrocarbon source fed to the autothermal reactor. For example in the event that the amount of $H_2$ recovered from the separated portion of make-up gas is reduced due to the deposition of carbonaceous product such as coke or soot over the catalytic surface in the WGS reactor, this reduction can be compensated by increasing the amount of $H_2$ recovered from loop purge.

**[0047]** Likewise, in the event that the feedstock should be changed to a hydrocarbon source characterised by a higher carbon-to-hydrogen ratio, the consequent reduction of the stoichiometric number can be compensated by increasing the amount of make-up gas fed to the HTS and related hydrogen recovery unit.

**[0048]** The hydrocarbon source is preferentially a light hydrocarbon source and more preferentially a natural gas. In an embodiment of the present invention, the hydrocarbon source may be subjected to hydrodesulfurisation, and subsequently to a first and to a second pre-reforming stage. Preferentially, the first pre-reforming is carried out in an adiabatic fixed-bed reactor at a temperature of approximately 350 to 530 °C; the secondary pre-reforming may be carried out in an adiabatic reactor at a temperature higher than that of the first pre-reforming reactor. Preferentially, the temperature of the second pre-reformer is approximately 500 to 750 °C.

**[0049]** Advantageously, treating the hydrocarbon source in a first pre-reformer and in a second pre-reformer that operates at a higher temperature over the first one, enables a high conversion of the high molecular weight hydrocarbons ($>C_2$) to methane in the pre-reformer and conversion of methane to syngas in the second pre-reformer thus deposition of soot over the catalyst surface in the autothermal reformer is avoided and the life span of the reforming catalytic is extended. Moreover, the oxygen requirement for the operation of the autothermal reformer is minimised due to the additional reforming duty adsorbed by the secondary pre-reformer.

**[0050]** In another embodiment, the hydrocarbon source is fed to the desulphurisation unit and subsequentially to a single pre-reformer before being feed to the autothermal reformer.

**[0051]** In another embodiment, the hydrocarbon source is fed to the desulphurisation unit and subsequentially to the autothermal reformer and no pre-reforming stage is employed.

**[0052]** The autothermal reforming may be fired with oxygen or enriched air produced in an air separation unit. A further aspect of the invention is the integration of such air separation unit with the other equipment. The high-pressure steam produced from cooling of the makeup gas may be used to operate the air separation unit, e.g. to power a steam turbine of the unit. A medium-pressure steam extracted from the air separation unit may be further used by injection upstream the pre-reformer, therefore serving as the process steam necessary in the reforming section. Advantageously, the totality of the steam produced in the process is exploited in the plant, therefore an improved design flexibility is envisaged in concomitant with an improved efficiency due to a reduction in the natural gas consumptions as a result of the employment of an autothermal reformer that operates at low steam to carbon S/C ratio.

**[0053]** Furthermore, the steam demand and production between the syngas generation and the methanol synthesis are decoupled to improve the operability and the flexibility of the plant.

**[0054]** A particularly preferred embodiment includes:

a light hydrocarbon feed is converted to syngas in the following steps: hydrodesulphurization, pre-reforming, secondary pre-reforming (at higher temperature), autothermal reforming;

the autothermal reforming is performed at low S/C ratios 0.5-1.5 and at a pressure of 25-60 bar, the inlet stream to the autothermal reformer consists of

the pre-reformed feed mixed with a portion of the HRU retentate;

the resulting syngas is cooled by raising high pressure steam;

a portion of the resulting fresh make-up gas is withdrawn and sent to a water-gas shift reactor, the water-gas shift effluent is then subjected to $H_2$ recovery by PSA;

the resulting stream of pure hydrogen, obtained from the PSA, is mixed with the remaining larger part of the fresh make-up gas and with a hydrogen enriched stream from a membrane HRU unit, to form an adjusted make-up gas that is fed to the synthesis loop compressor;

the compressed adjusted make-up gas is mixed with the recirculated recycle stream and fed to a methanol reactor;

the reactor effluent is cooled and a crude methanol is condensed and sent to a distillation section;

a purge stream is withdrawn from the unreacted gas mixture;

the remainder (and majority) of the unreacted gas mixture (recycle stream) is recycled through a recirculatory to the inlet of the methanol reactor, by mixing with the adjusted make-up gas;

the purge stream is sent to a membrane-based HRU, the retentate depleted of hydrogen is partly discarded and used as fuel, and partly recycled to the autothermal reformer;

the hydrogen enriched permeate is mixed with the fresh make-up gas and the pure $H_2$ from PSA to form the adjusted make-up gas.

**[0055]** According to still another aspect of the invention, the makeup gas has a low steam to dry gas (SIOG) ratio. For example this ratio in in the range 0.1 to 0.5. In case of a makeup gas with such low S/DG ratio the shift reaction is preferably performed over an iron-free catalyst.

**[0056]** The preferred embodiments of the invention give among others the following advantages: consumption is low due to the low S/C used in the front-end; the requirement of oxygen for the operation of the autothermal reformer can be minimized thanks to the additional reforming duty absorbed by the secondary pre-reforming; the production of steam can be limited due to the low S/C used in the front-end so that no steam must be exported.

**[0057]** The steam network may be arranged in order to take advantage of the low steam production. In particular, steam demand and production between the syngas generation and the methanol synthesis sections of the plant can be decoupled, thus increasing the plant operability and modularity.

**[0058]** Preferably the crude methanol extracted from the methanol synthesis loop is refined to high purity methanol by a distillation scheme comprising four columns. Preferably, the four columns comprise a topping column for the removal of volatile components present in the crude, and three refining columns separating methanol from water and higher alcohol by-products. Advantageously, the four columns distillation layout yields refined methanol by using a smaller amount of steam for reboiling. The decreased steam is necessary to capitalize on the reduced gas consumption and steam production provided by the low S/C front end.

**[0059]** Preferably, the pressure levels of the three columns are respectively in the ranges of 12 to 16 bar, 6 to 10 bar and 0.5 to 3 bar. Advantageously, the related heat necessary for reboiling can be provided at a temperature level compatible with low-pressure steam obtained from the operation of the steam turbines.

**[0060]** Even more advantageously, the amount of reboiling duty for the distillation recovered from the make-up gas cooling may be minimised and limited to the topping reboiling duty. Refining duty may be obtained from the condensation of steam extracted from the operation of a steam turbine. Consequently, the steam demand and production between the syngas generation and the methanol synthesis sections of the plant may be decoupled and the plant operability and modularity may be increased.

**[0061]** In an embodiment, the high-pressure steam produced in the syngas cooling section/zone is utilised to operate an air separation unit that provides pure oxygen fed to the autothermal reformer. Medium pressure steam may be extracted from the steam turbine of the air separation unit and utilised in part as process steam to carry out the reforming reactions of the syngas generation section, and in another part to operate further steam turbines for plant services.

**[0062]** In an embodiment of the invention, the steam generated by heat exchange in the methanol synthesis reactor is superheated in a fired heater and utilised to operate the adjusted make-up gas compressor and the recycle stream recirculatory. Preferably, low-pressure steam is extracted from the make-up gas compressor steam turbine and condensed in the primary reboiler of the first refining column.

__Description of the figures__

**[0063]** Fig. 1 shows a methanol synthesis process according to an embodiment of the invention.

**Detailed description of the preferred embodiments**

**[0064]** Fig. 1 illustrates a scheme 150 of a plant for producing methanol 56 from a light hydrocarbon 101, e.g. natural gas.

**[0065]** The hydrocarbon 101 is supplied via line 40 to a hydrodesulfurisation unit 41 and the sulfur-free hydrocarbon 42 is fed to a first pre-reformer 43 wherein high molecular weight hydrocarbons ($\geq C_2$) are partially converted into methane, hydrogen and carbon oxides.

**[0066]** The gas mixture 44 leaving the pre-reforming is then fed to a second pre-reformer 45 wherein further conversion of the hydrocarbons is carried out yielding a hydrocarbon-containing gas 1 predominantly comprising methane, hydrogen and carbon oxides.

**[0067]** The hydrocarbon containing gas 1 is fed with an oxygen-containing gas 25 to an autothermal reformer 2 to yield a make-up gas 3 having a sub-stoichiometric contend of hydrogen, that is a hydrogen deficit over a stoichiometric number prescribed by the methanol reaction.

**[0068]** The oxygen-containing gas 25 is obtained from an air separation unit 47. The air separation unit 47 is operated with high-pressure stream 52 obtained in a makeup gas cooling zone 60. A medium-pressure steam 48 discharged by the air separation unit 47 is introduced in the first pre-reformer 43 and used as process steam further down the line (not shown).

**[0069]** The hot make-up gas 3 exiting the reformer 2 is fed to a cooling zone 60 which, in the shown embodiment, includes a first heat exchanger section 4 and a second heat exchanger section 8.

**[0070]** In the first heat exchanger section 4, the hot make-up gas 3 is cooled to yield a partially cooled make-up gas 5 and the high-pressure stream 52 is produced.

**[0071]** A minor fraction 26 of the partially cooled make-up gas 5 is separated from an intermediate point 6 of the cooling zone 60, namely after passage in the first heat exchanger section 4 and before entering the second heat exchanger section 8. Said separated portion 26 is sent to a train including a HTS shift reactor 27, a cooling section 57 and a PSA unit 33 for separation of a hydrogen stream 34. The separated stream 26 is preferably about 2% of the makeup gas 5.

**[0072]** The remaining portion 7 of makeup gas (after separation of the above fraction 26) is sent to the second heat exchanger section 8 where it is further cooled obtaining a stream 9 of fully cooled makeup gas.

**[0073]** More in detail the separated makeup gas 26 is fed to the high-temperature shift reactor 27 to yield a shifted gas 28 enriched in hydrogen. Said shifted gas 28 is then cooled in the cooling section 57 comprising a first heat exchanger 29 and a second heat exchanger 31. The effluent 30 of the first heat exchanger 29 is further cooled in the second heat exchanger 31. The so obtained cooled gas 32 is fed to the pressure swing adsorption unit 33 to yield the hydrogen stream 34 and a tail gas 35 comprising methane and carbon dioxides. Said tail gas 35 may be sent to combustion.

**[0074]** The temperature of the make-up gas 3 leaving the autothermal reformer 2 may be about 1000 °C. The temperature of the separated make-up gas 26 at the inlet of the high-temperature water gas shift reactor 27 is typically about 350 °C. The temperature of the shifted gas 28 leaving the water gas shift reactor 27 may be about 470 °C and the temperature of the cooled gas 32 entering the pressure swing adsorption unit 33 after proper cooling is of about 45 °C.

**[0075]** The fully cooled make-up gas 9 is mixed at a mixing point 10 with at least a portion of the hydrogen stream 34 and with a permeate 20 rich in hydrogen which is recovered from the loop purge as described below. By mixing with the hydrogen stream 34 and permeate 20, the content of hydrogen in the makeup gas 9 is adjusted, i.e. the initial lack of hydrogen is compensated.

**[0076]** Typically, a hydrogen stream obtainable in a PSA unit has a high purity. It should be noted the hydrogen stream 34 may contain unavoidable impurities.

**[0077]** The so obtained adjusted make-up gas 11 after compression in a syngas compressor 12 is fed to a methanol synthesis loop 14.

**[0078]** In some embodiments the hydrogen stream 34 leaving the pressure swing adsorption unit 33 may be fed directly to the mixing point 10 of the main line, i.e. no compression stage is required as the hydrogen stream 34 is extracted at a sufficient pressure.

**[0079]** A condensate crude methanol stream 15 and a purge stream 16 are extracted from the methanol synthesis loop 14. The condensate crude methanol stream 15 is purified in a distillation section 49 to yield a pure methanol stream 56.

**[0080]** Preferably the distillation section 49 includes four distillation columns operating in cascade. Particularly preferably the four-column setup described in EP 2 617 478 may be adopted, which has the advantage of a low consumption of steam.

**[0081]** The purge stream 16 after suitable cooling in a heat exchanger 17 is fed to a membrane-based hydrogen purification system 19 obtaining a permeate 20 rich in hydrogen and a retentate 21 rich in methane. Typically, the $H_2$ recovery in the hydrogen purification system 19 is carried out so that the recovered $H_2$ stream 20 is at a pressure compatible with direct mixing with stream 9.The permeate 20 rich in hydrogen is recirculated back to the mixing point 10 where it concurs to adjustment of the hydrogen content in the makeup gas 9.

**[0082]** At least a portion of the retentate 21 may be fed, after cooling in a heat exchanger 24, to the reformer 2 and used as an additional feedstock for the synthesis of the make-up gas 3. The recycle of the retentate 21 rich in methane tackles the problem of the methane slip and avoid the saturation of the heating duty by the waste gases of the plant. A portion 22 of the retentate may be separated and sent to combustion.

# REFERENCES CITED IN THE DESCRIPTION

Cited references



**Patent documents cited in the description**


- US6797252B [0012]
- GB2585477A [0016]
- EP2617478A [0080]

PATENTKRAV

1. Fremgangsmåde til fremstilling af metanol, der omfatter følgende trin:
   a. reformering af en carbonhydridholdig kilde til en syntesegas (3) omfattende hydrogen, carbonoxider og vand;
   b. udsættelse af syntesegassen (3), der er genereret i trin (a), for en afkølingsproces;
   c. separation af en andel (26) af syntesegas under afkølingsprocessen i trin b) og før afkølingsprocessen er gennemført, og udsættelse af den tilbageværende andel (7) af syntesegas for komplet afkøling, så der opnås en hovedstrøm af syntesegas (9), idet den separerede gas (26) har en højere temperatur end hovedstrømmen (9);
   d. udsættelse af den separerede syntesegas (26) for mindst ét water-gas-shift (WGS) konverteringstrin (27), så der opnås en konverteret gas (28), der er beriget med hensyn til hydrogen;
   e. afkøling af den konverterede gas (28) og tilførsel af den afkølede konverterede gas (32) til en første hydrogengenindvindingssektion (33), så der opnås en første hydrogenstrøm (34);
   f. tilsætning af hovedstrømmen af syntesegas (9) med den første hydrogenstrøm (34) og med en anden hydrogenstrøm (20), der er opnået i trin (i), således at der opnås en justeret syntesegas (11) med et justeret indhold af hydrogen;
   g. tilførsel af den justerede syntesegas (11) til et metanolsyntese-loop (14), hvori der udføres katalytisk omdannelse af carbonoxider til metanol under metanolsynteseforhold, så der opnås en kondensat-råmetanolstrøm (15);
   h. oprensning af kondensat-råmetanolstrømmen (15), fortrinsvis i en destillationssektion (49), så der opnås et metanolprodukt (56);
   i. tilførsel af en rensestrøm (16), der er trukket ud af metanolsyntese-loopet, til en anden hydrogengenindvindingssektion (19), så der opnås en anden hydrogenstrøm (20) indeholdende hydrogen, der er fjernet fra rensestrømmen, og en slutgas (21) indeholdende metan;

j. tilsætning af den anden hydrogenstrøm (20) til hovedstrømmen af syntesegas (9) ifølge trin (f);

k. anvendelse af mindst en andel af slutgassen (21) som råmateriale til fremstilling af syntesegassen (3) i trin (a).

2. Fremgangsmåde ifølge krav 1, hvor den separerede andel (26) af syntesegas er en mindre andel.

3. Fremgangsmåde ifølge krav 2, hvor den volumetriske strømningshastighed af den separerede andel af syntesegas (26) ikke er større end 15 % af den samlede volumetriske strømningshastighed af syntesegassen (3), fortrinsvis 1 % til 10 %.

4. Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 3, hvor afkølingsprocessen i trin c) udføres i en kølesektion (60), der omfatter en flerhed af varmevekslere, der er indrettet i serie, og den separerede andel (26) af syntesegas separeres efter passagen i mindst én af varmevekslerne.

5. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor reformeringen i trin a) indbefatter autotermisk reformering, eventuelt efter forudgående præ-reformering.

6. Fremgangsmåde ifølge krav 5, hvor den autotermiske reformering udføres ved et vanddamp-til-carbon-forhold (S/C), der er omfattet mellem 0,5 og 1,5, fortrinsvis mellem 0,8 og 1,2.

7. Fremgangsmåde ifølge krav 5 eller 6, hvor den autotermiske reformering udføres ved et absolut tryk mellem 25 og 60 bar, fortrinsvis mellem 35 og 50 bar.

8. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor water-gas-shift-konverteringen i trin d) indbefatter højtemperatur-konvertering, fortrinsvis mellem 300 og 500 °C, mere fortrinsvis mellem 350 og 450 °C.

9. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor den første hydrogengenindvindingssektion (27) indbefatter en pressure-swing-adsorptionsenhed.

10. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor den anden hydrogengenindvindingssektion (19) indbefatter en membranbaseret hydrogengenindvindingsenhed.

11. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor en andel af den første hydrogenstrøm (34) anvendes som brændsel til opfyldelse af fremgangsmådens energibehov og/eller som råmateriale til samproduktion af ammoniak.

12. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor den carbonhydridholdige gas er opnået fra en naturgaskilde (101) ved hydroafsvovlning (41), præ-reformering (43) og sekundær præ-reformering (45), hvor den sekundære præ-reformering (45) udføres ved en temperatur, der er højere end præ-reformeringen (43).

13. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor reformeringen i trin a) udføres med oxygen eller en oxygenholdig strøm, der er produceret i en luftseparationsenhed (47), og en vanddamp (52), der er genereret i syntesegasafkølingen i trin b), anvendes til at drive luftseparationsenheden.

14. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor syntesegassen (3), der er opnået i reformeringsprocessen, har et vanddamp-til-tørgas-forhold, der ikke er større end 0,5, fortrinsvis 0,1 til 0,5.

15. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor oprensningen af kondensat-råmetanolstrømmen (15) i trin (h), udføres i en

destillationssektion (49) omfattende fire kolonner, der opererer i kaskade, hvor en af de fire kolonner er en topping-kolonne til fjernelse af flygtige bestanddele, og de andre tre kolonner er raffineringskolonner, der er udformet til at separere metanol fra vand og højere alkohol-biprodukter.

16. Anlæg til fremstilling af metanol ud fra en syntesegas indeholdende hydrogen, carbonoxider og eventuelt inerte bestanddele, som omfatter:

a) en reformeringssektion, der er egnet til reformering af en carbonhydridholdig kilde til en syntesegas (3) omfattende hydrogen, carbonoxider og vand;

b) en kølesektion, der er indrettet til afkøling af den syntesegas (3), der er genereret i trin (a);

c) en linje, der er indrettet til at separere en andel (26) af syntesegassen fra en mellemplacering af kølesektionen og før komplet afkøling, og en linje, der er indrettet til at udsætte den tilbageværende andel (7) af syntesegas for komplet afkøling i sektionen, så der opnås en hovedstrøm af fuldt afkølet syntesegas (9) ved en temperatur, der er lavere end den separerede syntesegas (26);

d) en water-gas-shift-sektion (27), der er forbundet med linjen, der fører den separate andel af syntesegas (26) og er konfigureret til at producere en konverteret gas (28), der er beriget med hensyn til hydrogen;

e) en kølesektion af den konverterede gas og en første hydrogengenindvindingssektion (33), der er indrettet til at modtage den konverterede gas efter afkøling og til at producere en første hydrogenstrøm (34);

f) en linje, der er indrettet til at tilsætte den første hydrogenstrøm (34) til hovedstrømmen af syntesegas (9), og en linje, der er indrettet til at tilsætte en anden hydrogenstrøm (20) opnået i trin (i) til syntesegassen, således at der opnås en justeret syntesegas (11) med et justeret indhold af hydrogen;

g) et metanolsyntese-loop (14) og en linje, der er indrettet til at tilføre den justerede syntesegas (11) til loopet, hvori der udføres katalytisk omdannelse af carbonoxider til metanol under metanolsynteseforhold, så der opnås en kondensat-råmetanol (15);

h) en oprensningssektion af kondensat-råmetanolen (15), fortrinsvis en flerkolonne-destillationssektion (49), som opnår metanol (56);

i) en anden hydrogengenindvindingssektion (19), der er indrettet til at modtage en rensestrøm (16), der er trukket ud af metanolsyntese-loopet, og til opnåelse af den anden hydrogenstrøm (20) og en slutgas (21) indeholdende metan, der er fjernet fra rensestrømmen;

j) en linje, der er indrettet til at tilføre mindst en andel af slutgassen (21) som råmateriale til reformeringssektionen til fremstilling af syntesegassen (3).

17. Anlæg ifølge krav 16, der indbefatter en eller flere af følgende:
reformeringssektionen indbefatter en autotermisk reformeringsenhed, eventuelt med en eller flere præ-reformeringsenhed(er);
den første hydrogengenindvindingssektion er en PSA-enhed;
den anden hydrogengenindvindingssektion er en membranseparationsenhed;
water-gas-shift-sektionen af den separerede syntesegas indbefatter en højtemperatur-konverteringsreaktor.

18. Anlæg ifølge krav 16 eller 17, hvor oprensningssektionen af kondensat-råmetanolen (15) i trin (h) omfatter fire kolonner, der opererer i kaskade, hvor en af de fire kolonner er en topping-kolonne til fjernelse af flygtige bestanddele, og de andre tre kolonner er raffineringskolonner, der er udformet til at separere metanol fra vand og højere alkohol-biprodukter.

# DRAWINGS

Drawing

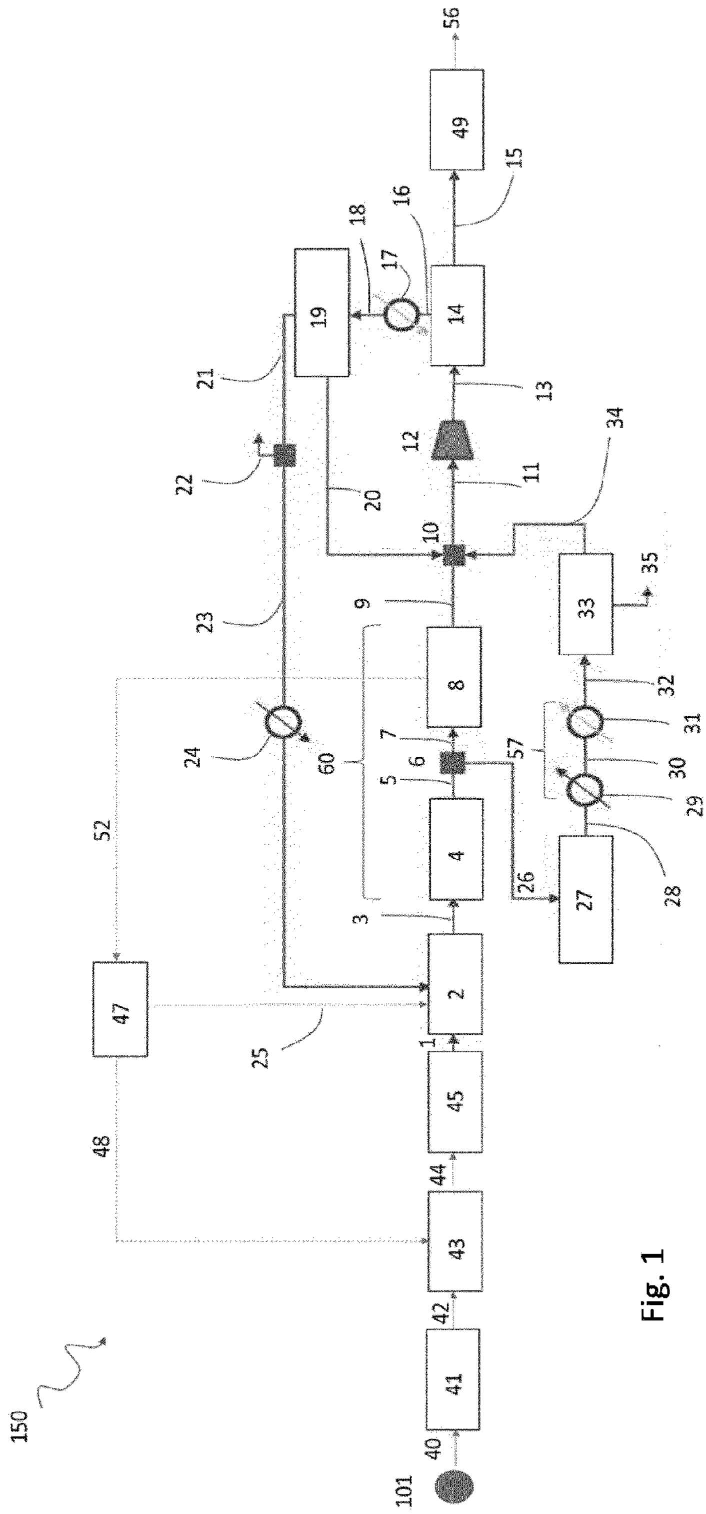


Fig. 1