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- (54) Benævnelse: **FREMGANGSMÅDE OG ANLÆG TIL SYNTETISK NATURGAS**
- (56) Fremdragne publikationer:
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DESCRIPTION

Field of the invention

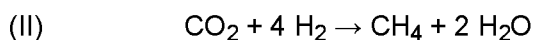
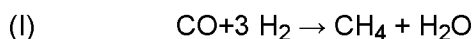
[0001] The invention relates to a process for producing substitute natural gas (SNG). The invention, in particular, relates to a process for producing SNG by reacting a synthesis gas comprising hydrogen and carbon oxides in a methanation section comprising adiabatic reactors with intermediate heat recovery and gas recirculation. The invention also relates to a plant operating with such process.

Prior art

[0002] Interest in the technical field of SNG production is continuously rising. SNG is a clean fuel which can be distributed with existing natural gas pipelines and facilities, and can be used as a substitute of natural gas in a wide range of applications.

[0003] A known process to produce substitute natural gas (SNG) involves methanation of a synthesis gas (make-up syngas) comprising hydrogen and carbon oxides. By the reaction of methanation, the make-up syngas is converted in a more valuable product consisting of 95% or more of methane (CH₄) with small amounts of carbon dioxide, hydrogen and inerts. The syngas may be obtained from coal or biomass gasification with further advantages: SNG from coal gasification is attractive because of large availability of coal, while SNG from biomass gasification gives no contribution to the CO₂ global emissions compared to fossil fuels.

[0004] Basically, the process of methanation of the syngas involves the following, strongly exothermal reactions:



where reaction (I) has a thermal output (enthalpy of reaction) of around 206 kJ/mol and reaction (II) of around 165 kJ/mol.

[0005] According to known art, the above reactions are carried out in a so-called methanation section comprising a plurality of adiabatic reactors with heat recovery and gas recirculation.

[0006] The reactors are disposed to operate in series, i.e. the fresh gas is fed to the first reactor and each of the subsequent reactors is fed with a partially-converted gas stream taken from the previous (upstream) reactor of the section. The reactors contain an appropriate catalyst to increase the yield of the reaction.

[0007] Heat recovery and gas recirculation are used to keep the exothermal reactions under control and avoid an excessive temperature inside reactors, that may damage the reactor itself and/or the catalyst. More in detail, heat recovery is provided by heat exchangers cooling the hot gas stream at the outlet of each reactor e.g. by producing high pressure steam. Recirculation is a further measure to control the reaction rate and the temperature inside the reactors, by dilution of the fresh syngas fed to the first reactor with a portion of the reacted gas. The gas recirculation requires the provision of an appropriate compressor.

[0008] For example, a well known process marketed under the name TREMP™ involves a methanation section comprising a first reactor fed with fresh syngas having appropriate hydrogen to carbon monoxide ratio, and two further reactors. Reacted gas at the output of the first reactor passes through a super heater and a high pressure boiler and is split into two streams. One stream is directed to the second reactor, and the other stream is recirculated to the inlet of the first reactor via a gas preheater and a compressor. In another known process, a recirculation gas flow is taken downstream a second or subsequent reactor, and mixed with the fresh gas fed to the first reactor, i.e. the recirculation loop comprises all the reactors of the méthanation section, with the possible exception of the last (finishing) reactor.

[0009] A common feature of the prior-art processes is that the fresh gas input is entirely directed to the first reactor. Due to relevant heat output of the reaction, a strong dilution is required and, hence, a relevant portion of the reacted gas need to be re-circulated. The ratio between the total molar flow rate entering the first reactor and the molar flow rate of the fresh syngas feedstock can reach a value up to 6 or 7, meaning that about 15-20% or even less of the gas entering the first reactor is fresh syngas, while 80% or more is re-circulated reacted gas.

[0010] As a consequence, the power absorption of the compressor for gas recirculation is quite high and hence the compressor itself is a large and expensive item. Another drawback is that the amount of re-circulated gas increases the flow rate through the reactors, especially the first one, requiring larger and more expensive units and a larger quantity of catalyst.

[0011] All these drawbacks affect the cost of the methanation section and then the competitiveness of the price of the SNG over the fossil natural gas; on the other hand, the above high value of re-circulation ratio appears indispensable in the prior art to avoid overheat of the reactors. Processes for producing SNG are for instance disclosed in US-A-4 133 825 and GB-A-2 060 686.

Summary of the invention

[0012] The problem underlying the invention is to provide a more cost-effective and competitive process for converting a syngas containing carbon oxides and hydrogen into

substitute natural gas. More in detail, the invention aims to reduce the need of gas recirculation and related drawbacks still affecting the prior-art processes.

[0013] The basic idea of the invention is to feed the fresh make-up syngas in parallel to the reactors of the methanation section. Hence, the above problem is solved with a process for producing SNG from a fresh syngas feedstock as recited in attached claim 1. According to the invention, gas recirculation is carried out by taking a portion of the gas stream at the outlet of the first reactor and feeding said gas portion to the same first reactor. In other words, according to the invention the gas recirculation loop involves the first reactor only, which is fed with fresh syngas added with re-circulated reacted gas, while each of the second and further reactors is fed with fresh syngas added with the reacted gas coming from the previous reactor of the methanation section.

[0014] In a preferred embodiment, the fresh make-up syngas feedstock is split into a plurality of fresh gas streams and each of said fresh gas streams is fed to a respective one of said reactors of the methanation section. More preferably, each of said fresh gas streams is between 15% and 35% of the total available syngas.

[0015] Typical arrangement is with four main reactors in series with the fresh make-up gas split 25% to the first reactor, 20% to the second, 25% to the third and 30% to the fourth, The number of reactors depends on the type of catalyst that is used (allowable maximum outlet temperature) and the quality of gas that is required (maximum amount of CO₂ and H₂).

[0016] According to other aspects of the invention, steam is added at the inlet of at least the first reactor, and preferably also at the inlet of the second reactor of the methanation section. Steam addition is effective in controlling the reaction temperature because the steam dilute the fresh syngas and shifts the chemical equilibrium reducing the reaction rate inside the reactors, being one of the products of reactions (I) and (II).

[0017] In a preferred embodiment, reacted gas from the first reactor is split into a first gas portion and a second gas portion; said first gas portion is re-circulated to dilute the fresh gas stream fed to the first reactor, obtaining a diluted gas stream at the inlet of said first reactor which is further diluted by addition of a steam flow before entering the first reactor; said second gas portion is used to dilute the fresh gas fed to a second reactor of the methanation section, and also the gas flow entering said second reactor is further diluted with steam. Steam can be added before or after dilution or the fresh gas with the re-circulated or reacted gas.

[0018] An object of the invention is also a methanation section for converting a syngas containing carbon oxides and hydrogen into substitute natural gas, operating with the above process.

[0019] recited in attached claim 9. More preferably, steam addition lines are provided to further dilute the gas entering the first and second reactor of the methanation section.

[0020] The invention has the following advantages. As the first reactor receives only a portion of the fresh gas feedstock, the temperature inside can be controlled with a lower gas recirculation compared to prior art, e.g. with total to fresh gas molar ratio ~ 2 . The need of recirculating the reacted gas is further decreased by the steam addition of preferred embodiments of the invention. Each of the second and further reactors receives a portion of the fresh gas diluted with the partially converted gas coming from the upstream reactor of the methanation section, so that there is no need to provide gas recirculation also to said reactors.

[0021] Thanks to the invention, the compressor of the recirculation loop is much smaller than the compressor required in the prior art. For example a plant operating with a prior-art process and capable of $2 \cdot 10^6$ Nm³/day of SNG typically requires a 8-MW compressor for gas recirculation, while a plant operating with the inventive process and capable of the same output would require a much less expensive 350-kW compressor.

[0022] A further advantage is that due to the partition of the fresh gas and the reduced gas recirculation, there is a less flow rate through the reactors of the methanation section and especially at the inlet of the first compressor. Hence, the invention allows to use smaller units and a less quantity of catalyst is required for each reactor.

[0023] It is to be noted that the heat recovery is not affected by the invention, i.e. the production of high pressure superheated steam is the same as a prior-art process.

[0024] All the above advantages make the SNG more competitive over fossil natural gas or other fuels. The invention is particularly useful to produce SNG from biomass or coal gasification.

[0025] The features and advantages of the present invention will be more evident from the following description of preferred indicative and nonlimiting embodiment examples, with reference to the attached figures.

Brief description of the figures

[0026] Fig. 1 is a schematic layout of a plant operating with the inventive process.

Detailed description of a preferred embodiment

[0027] With reference to Fig. 1, a methanation section for SNG production is globally indicated as 10, and receives a feedstock 11 of a fresh syngas containing carbon oxides and hydrogen. Said fresh syngas stream 11 can be obtained for example in a coal or biomass gasification section (not shown).

[0028] The methanation section 10 comprises a series of adiabatic reactors 101-104 with recovery heat exchangers 201-204. Reactors 101 to 104 are *per se* known, for example axial or axial-radial flow reactors with an appropriate catalyst, operating at around 35 bar pressure with inlet gas temperature between 240 and 300 °C and outlet gas temperature around 600 °C. Heat exchangers 201 to 204 receive the hot gas from reactors 101 to 104, respectively, and may operate as HP steam boilers or provide water pre-heating or steam superheating, according to the needs. Hot water/ steam line of exchangers 201 to 204 is not shown in the figure for simplicity.

[0029] Syngas stream 11 is fed in parallel to reactors 101 to 104, as shown. The syngas feeding line of the methanation section 10 provides a split of the stream 11 into a feeding stream 12 directed to the first reactor 101 and a feeding stream 13 which is further partitioned into feeding lines 14, 15 and 16 directed to reactors 102, 103 and 104 respectively. Preferably, each of said gas streams 12 to 16 is between 15 and 35% molar flow rate of total syngas feedstock 11.

[0030] The gas stream 12, before entering the first reactor 101, is diluted with re-circulated gas stream 24 and fed to a preheater 17. The resulting diluted and preheated stream 18 is added in the example with steam from line 19 to further dilute the fresh syngas, and then introduced into the reactor 101.

[0031] Output gas stream 20 from the reactor 101, which is partially converted into methane and has a high temperature, e.g. 600 °C, as a result of the exothermal methanation reactions, is cooled in the heat exchanger 201 obtaining a cooled reacted gas stream 21.

[0032] A first portion 22 of said cooled gas stream 21 is re-circulated to the reactor 101 via a recirculation loop 40 comprising a compressor 23. More in detail, the gas stream 22 is passed through pre-heater 17 to preheat the gas stream entering the reactor 101, and fed to the compressor 23. The re-circulated gas stream 24 delivered by compressor 23, as stated above, is used to dilute the fresh syngas portion 12 directed to the reactor 101.

[0033] Preferably, the ratio between the total flow of stream 18 entering the first reactor 101, and the fresh gas fed to the same reactor 101 via gas stream 12, is around 2 mol/mol.

[0034] A second portion 25 of the first reactor output stream 21 is mixed with the fresh make-up gas stream 14, and further added with steam via line 26, thus obtaining a diluted feeding gas stream 27 of the second reactor 102. Outlet gas stream 28 of said second reactor 102 is cooled in the heat exchanger 202 and the cooled gas stream 29 is fed to the third reactor 103 together with the fresh gas stream 15. In a similar way, cooled gas stream 30 from reactor 103 is mixed with the fresh gas 16 and fed to fourth reactor 104.

[0035] It should be noted that steam can be added before or after dilution of the fresh gas with the re-circulated or reacted gas. Preferably steam 19 is added to the diluted and preheated flow 18, as shown; steam 26 can be added to fresh gas 14 or to fresh gas 14 diluted with the

reacted gas portion 25.

[0036] Outlet 32 of fourth reactor 104 is cooled in the heat exchanger 204 and sent to a separator 110 obtaining a SNG stream 34 and a condensate 33; the SNG stream 34 may be directed to a further, so-called finishing reactor. Removing the condensate 33 before feeding the SNG to the finishing reactor is preferred in order to have a more valuable final product.

[0037] The SNG typically is composed of 95% or more of methane (CH₄) with small percentages of carbon dioxide, hydrogen and inerts. The SNG obtained can be used for any purpose.

[0038] A detailed example is now disclosed. In a methanation section 10, as shown in Fig. 1, 435.000 Nm³/h of make up gas @ 37 °C are fed at 11, and a flow 12 of 109.000 Nm³/h is fed to first reactor 101. The remaining part is divided into 88.000, 111.000 and 127.000 Nm³/h respectively to reactors 102, 103 and 104. A flow of 35.000 kg/h of steam @ 450 °C is added at 19 and a 20.000 kg/h of steam at the same temperature are added at 26, while 117.400 Nm³/h of steam-diluted syngas are recycled at 22 and merged with make-up gas 12 via line 24. Around 230.000 Nm³/h of SNG are obtained at stream 34. Temperature at the outlet of reactors is around 600 °C.

[0039] The methanation section 10 can be a subsection of a plant for producing SNG from a suitable source, e.g. coal or biomass, said plant including further subsections like a gasifier, air separation unit (ASU), CO shift converter to provide appropriate ratio between hydrogen and CO content of the syngas, acid gas removal, and so on. It should be noted that particulars of the methanation section 10 such as valves, pumps, auxiliaries, etc. are not shown as they are well known to the skilled person.

REFERENCES CITED IN THE DESCRIPTION

Cited references

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Patent documents cited in the description

- US4133825A [0011]
- GB2060686A [0011]

Patentkrav

1. Fremgangsmåde til fremstilling af syntetisk naturgas ud fra et råmateriale af frisk syntesegas (11), hvilken fremgangsmåde mindst omfatter trinnene til reaktion af den
5 friske syntesegas i et methaniseringsafsnit (10), som omfatter mindst en første adiabatisk reaktor (101) og en flerhed af yderligere adiabatisk reaktorer (102-104), som er serieforbundet, således at hver af flerheden af yderligere reaktorer (102-104) tilføres en gasstrøm, som tages fra den foregående reaktor i methaniseringsafsnittet, og recirkulering af mindst en del (22) af den reagerede gas som indgangsgas til mindst
10 én af reaktorerne, **kendetegnet ved, at** råmaterialet af frisk syntesegas (11) tilføres parallelt til reaktorerne (101-104), og trinnet til gasrecirkulering udføres ved at tage en del (22) af den reagerede gasstrøm (20) fra den første reaktor (101) og anvende denne gasdel (22) som en recirkuleret gas til at fortynde den strøm (12) af frisk gas, som tilføres den første reaktor (101), hvorved der opnås en fortyndet gasstrøm (18) ved
15 indløbet til den første reaktor.
2. Fremgangsmåde ifølge krav 1, hvor råmaterialet af frisk syntesegas (11) opdeles i en flerhed af strømme (12, 14, 15, 16) af frisk syntesegas, idet hver strøm af frisk gas tilføres til hver sin reaktor (101-104).
20
3. Fremgangsmåde ifølge krav 2, hvor hver af strømmene (12, 14, 15, 16) af frisk gas er på mellem 15 og 35 molprocent af det samlede gas-råmateriale (11).
4. Fremgangsmåde ifølge krav 1, hvor delen (22) af reageret gasstrøm tilføres den
25 første reaktors (101) indløb via en recirkulationssløjfe (40), der omfatter en kompressor (23) til den recirkulerede gasstrøm (22) og en forvarmer (17) til opvarmning af den fortyndede gasstrøm, før den strømmer ind i den første reaktor (101).

5. Fremgangsmåde ifølge krav 1 eller 4, hvor molforholdet mellem den samlede fortyndede gasstrøm (18), der strømmer ind i den første reaktor 101, og strømmen (12) af frisk gas, der tilføres den første reaktor (101), er omkring 2.
- 5 6. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor damp tilføres ved indløbet af mindst den første reaktor (101) for at fortynde indløbsgassen yderligere.
7. Fremgangsmåde ifølge krav 6, hvor reageret gas (21) fra den første reaktor (101)
10 opdeles i en første gasdel (22) og en anden gasdel (25), hvor den første gasdel (22) recirkuleres, således at strømmen (12) med frisk gas, som tilføres den første reaktor (101), fortyndes, hvorved der opnås en fortyndet gasstrøm (18) ved den første reaktors indløb, idet den fortyndede gasstrøm (18) fortyndes yderligere ved tilsætning af en dampstrøm (19), før gasstrømmen strømmer ind i den første reaktor (101), og den
15 anden gasdel (25) anvendes til at fortynde frisk gas (14), der tilføres en anden reaktor (102) i methaniseringsafsnittet (10), og den gasstrøm, der strømmer ind i den anden reaktor (102), fortyndes yderligere med damp (26).
8. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor
20 reaktorerne virker ved et tryk på omkring 35 bar.
9. Methaniseringsafsnit (10) til at omsætte en syntesegas (11), der indeholder carbonoxider og hydrogen, til en syntetisk naturgas (31) ifølge fremgangsmåden i et hvilket som helst af kravene 1 til 8, hvor methaniseringsafsnittet omfatter en første
25 reaktor (101) og en flerhed af yderligere reaktorer (102-104), der er tilpasset til at udføre en methaniseringsreaktion af den friske syntesegas (11), en tilførselsledning til frisk syntesegas, som er indrettet til at tilføre den friske syntesegas (11) parallelt til den første og de yderligere reaktorer, idet hver reaktor modtager en forudbestemt del (12, 14, 15, 16) af den friske syntesegas, og en recirkulationssløjfe (40), som modtager
30 en del (22) af reageret gas (21), der tages fra den første reaktor (101), og blander denne

del af reageret gas med den tilførte del (12) af frisk gas til den første reaktor (101), hvor gasrecirkulationssløjfen kun omfatter den første reaktor (101).

10. Methaniseringsafsnit ifølge krav 9, som yderligere omfatter
5 damptilsætningsledninger (19, 26) til yderligere fortynding af den gas, som strømmer ind i den første og den anden reaktor i methaniseringsafsnittet.

11. Methaniseringsafsnit ifølge et hvilket som helst af kravene 9 til 10, som omfatter
10 fire reaktorer (101-104), og hvor råmaterialet af frisk make-up-gas (11) opdeles i 25 % til den første reaktor (101), 20 % til den anden reaktor (102), 25 % til den tredje reaktor (103) og 30 % til den fjerde reaktor (104).

12. Methaniseringsafsnit ifølge et hvilket som helst af kravene 9 til 11, hvor de
adiabatiske reaktorer (101-104) er reaktorer med aksial eller aksial-radial strømning.

DRAWINGS

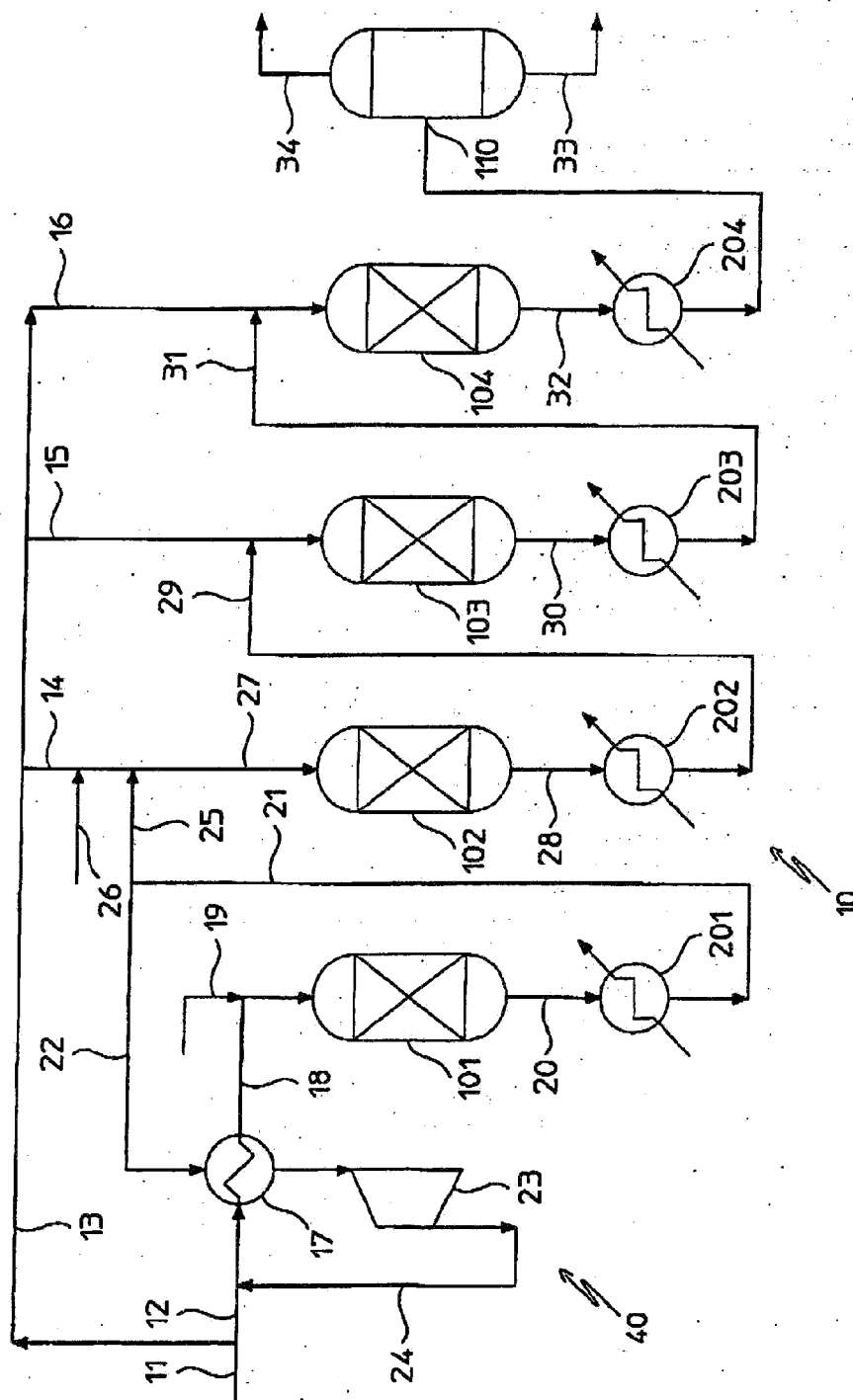


Fig. 1