



- (51) **International Patent Classification:**
C10L 3/08 (2006.01) *C10L 3/10* (2006.01)
- (21) **International Application Number:**
PCT/EP2016/055963
- (22) **International Filing Date:**
18 March 2016 (18.03.2016)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
PA 2015 00163 18 March 2015 (18.03.2015) DK
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- (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, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
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).

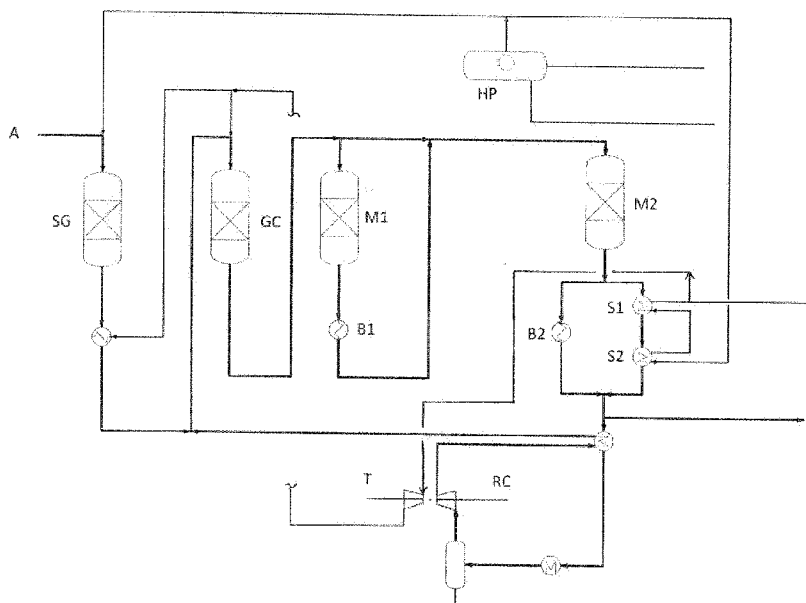
Declarations under Rule 4.17:

- 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:** A PROCESS FOR THE PRODUCTION OF METHANE AND POWER



(57) **Abstract:** In a process for the production of methane and power, including the steps of producing syngas from a carbonaceous feed, subjecting the syngas to methanation in two or more methanation reactors and producing superheated steam in one or more superheaters, a back pressure turbine is fed with the superheated steam to drive a recycle compressor, and all or some of the steam spent in the turbine is added to the methanation process to lower the potential for carbon formation and to save recycle compressor energy. This way, power can be generated at a lower price.

Title: A process for the production of methane and power

The present invention relates to a process for the production of methane and power. More specifically, the invention relates to the feeding of a turbine with superheated steam and use of the spent steam for process addition or heating, whereby power can be generated at a lower price than the normal production price.

A steam turbine is a device which extracts thermal energy from pressurized steam and uses it to do mechanical work on a rotating output shaft, i.e. a turbine uses steam to drive something, for example a pump, a compressor or a generator. Because a turbine generates rotary motion, it is particularly suited to drive an electrical generator. The steam turbine is a form of heat engine that derives much of its improvement in thermodynamic efficiency from the use of multiple stages in the expansion of the steam, which results in a closer approach to the ideal reversible expansion process.

Non-condensing or back pressure turbines are most widely used for process steam applications. The exhaust pressure is controlled by a regulating valve to suit the needs of the process steam pressure. Such turbines are commonly found at refineries where large amounts of low pressure process steam are needed.

A power plant facility having gas turbines, steam turbines and mixed gas/steam turbines is known from US 6.047.549 A. By use of appropriate networking of the three turbine facilities, an approach to isothermal heat supply and removal is achieved with optimal utilization of waste heat. Specif-

ically, the waste heat of the successively arranged turbine groups is used to generate high pressure stream, which is utilized in a back pressure turbine in such a way as to boost the efficiency.

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US 2010/0263607 A1 describes a system for generating steam for a turbine of an electric generator. The system includes a superheater which receives steam from a boiler and which superheats the steam. The superheated steam is then passed through a heat exchanger to transfer some of the heat energy in the superheated steam to a flow of water. This reduces the temperature of the superheated steam to a temperature which is suitable for the turbine. The water heated in the heat exchanger can be condensed water that has already passed through the turbine, and the water heated in the heat exchanger can be routed to the boiler, where it is recycled back into steam.

In US 2011/0120127 A1, a process for utilizing synthesis gas heat for the generation of supercritical steam in a low energy ammonia or methanol plant is disclosed. This process involves a reforming or partial oxidation stage, and the apparatus suitable for operating the process comprises at least one supercritical steam generator, at least one superheater, at least one back pressure turbine, at least one extraction and condensing turbine and at least one boiler feedwater pump. By the process, energy savings and overall cost advantages, i.e. better process economics, can be achieved.

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Finally, a combined multi-component gasification, methanation and power island steam turbine system is disclosed in

US 2010/0170247 A1. The gasification part includes a heat recovery design and associated controls for obtaining a desired steam to dry gas ratio, and the methanation part includes 1st, 2nd and 3rd methanation reactors and associated heat recovery integrated with high pressure, intermediate pressure and low pressure turbines and high pressure economizers. The power island steam turbine includes high pressure, intermediate pressure and low pressure turbines with an input coupled to an output of the superheaters in the methanation process. The subject-matter of this citation differs from that of the present invention in that the high pressure turbine and the recycle compressor are not connected and that no steam is added to the feed streams of any of the methanation steps.

The present invention differs from the prior art mentioned above in that it is used in applicant's SNG process where steam is consumed internally to heat up gas, or steam is added to the process gas to avoid carbon formation, more specifically "whisker carbon". In the process, SNG (substitute natural gas) is produced from cheap carbonaceous feedstocks, such as coal, petroleum coke, biomass or waste. SNG is rich in methane, and it can be used interchangeably with natural gas and distributed by the same means.

The conversion of the carbonaceous feed into SNG takes place in a number of process steps as follows:

- gasification of the feed to produce a gas rich in hydrogen and carbon monoxide,
- shift conversion to adjust the ratio between hydrogen and carbon monoxide,

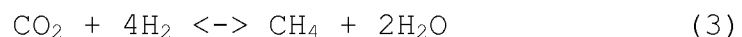
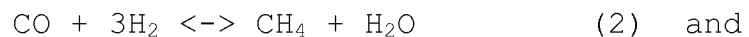
- acid gas removal, where carbon dioxide and hydrogen sulfide are removed in a washing process,
- methanation to convert carbon oxides and hydrogen to methane (SNG) followed by drying and possibly compression of the product SNG to pipeline conditions,
- production of oxygen for the gasification process in an air separation unit, and
- recovery of sulfur from the acid gas removal unit, which is most often done by converting the hydrogen sulfide to sulfur in a Claus unit according to the equation



If desired, the sulfur can subsequently be converted to concentrated sulfuric acid in a wet sulfuric acid (WSA) unit.

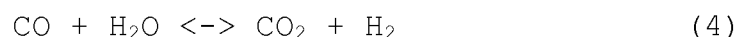
Methanation is the process where carbon oxides and hydrogen are converted to methane according to the reactions

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These reactions will be coupled to equilibrium between carbon monoxide and carbon dioxide as follows:

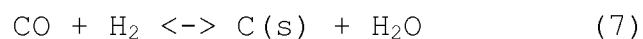
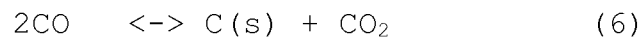
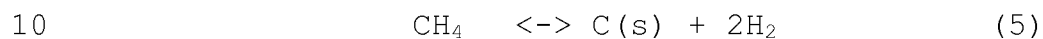
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Both reactions (2) and (3) are highly exothermic, releasing large amounts of reaction heat. Efficient recovery of the heat of reaction is essential for any industrial methanation technology.

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It is known from the field of steam reforming that catalysts may form carbon depending on the operation conditions and the actual catalyst formulation. Carbon may be formed on the catalyst either from methane, carbon monoxide or higher hydrocarbons. The formation of carbon from methane and carbon monoxide may be expressed by the following reactions:



The carbon formed depends on the operation conditions and the catalyst. Typically, carbon on a Ni-catalyst is in the form of whisker carbon. Said whisker carbon is described in the literature; see e.g. "Concepts in Syngas Manufacture" by J. Rostrup-Nielsen and Lars J. Christiansen, Catalytic Science Series vol. 10, 2011, pages 233-235. As mentioned, the choice of catalyst and operating conditions will determine whether or not carbon will form. According to the so-called principle of equilibrated gas, carbon will form if thermodynamics predict carbon formation from one or more of the reactions (5)-(7) after equilibration of reactions (2)-(4); see for example the above reference, pages 247-252. Means to avoid carbon formation in this case include reducing the temperature and increasing the steam content in the feed gas to the reactor.

30 The released heat from the above methanation reactions is most efficiently recovered as high pressure superheated steam.

The idea underlying the present invention is to feed a back pressure turbine with superheated steam and use the spent steam for process addition or heating. This way power can
5 be generated at a relatively low price because the condensation energy is exploited 100% in case of heating. In case of process addition of the steam it is seen - by comparison with addition of saturated steam and use of a condensing turbine - that the latter leads to an inferior utilization
10 of the energy.

Thus, the present invention relates to a process for the production of methane and power including the steps of producing syngas from a carbonaceous feed in a manner known
15 *per se* and subjecting the syngas to methanation in two or more methanation reactors after passage through a sulfur guard for desulfurization, wherein

- saturated steam is produced in one or more boilers and
20 fed to one or more superheaters to be converted to superheated steam,

- a back pressure turbine is fed with at least some of the superheated steam to drive a recycle compressor compressing
25 part of the effluent from the last methanation reactor, and

- all or some of the steam spent in the turbine is added to the methanation process to lower the potential for carbon formation and to save recycle compressor energy.

30 Utilization of superheated steam is essential in the present invention. Superheated steam is steam at a temperature

higher than its vaporization (boiling) point at the absolute pressure where the temperature is measured.

In a boiler, process waste energy is transferred to liquid water in order to create steam. In the boiler(s) used in the process of the invention, the water is always at the boiling point. Once the boiling point is reached, the temperature of the water ceases to rise and stays the same until all the water is vaporized. The water goes from a liquid state to a vapor state and receives energy in the form of latent heat of vaporization. As long as there is some liquid water left, the temperature of the steam is the same as that of the liquid water. The steam is then called saturated steam.

When all the water is vaporized, any subsequent addition of heat raises the temperature of the steam. When steam is heated beyond the saturated steam level, it is called superheated steam.

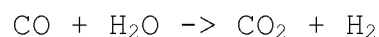
Industries normally use saturated steam for heating, drying or other procedures. Superheated steam is used almost exclusively for turbines to drive generators, compressors, pumps etc.

The back pressure turbine is utilized to drive a recycle compressor. Normally compressor drivers are electrical in SNG plants because of the relatively low power consumption. Even so, the power consumption in the process of the invention is lower; in fact it is zero.

The feed gas is preferably a gas in which the combined concentration of hydrogen and carbon oxides is at least 60%.

The inventive process is illustrated in the figure. The
5 syngas feed (A), which preferably comprises at least 7
mole% on dry basis of methane, more preferably at least 11
mole% on dry basis of methane and most preferably at least
15 mole% on dry basis of methane, is passed through a sul-
fur guard (SG) followed by a gas conditioning reactor (GC)
10 together with a small amount of water. The water can be -
but is not necessarily - high pressure steam HP. It is also
possible to use a small amount of liquid water, which sub-
sequently evaporates in the piping upstream the reactor.

15 In the gas conditioning reactor (GC), a shift reaction



takes place with the purpose of raising the temperature to
20 around 320°C. At lower entry temperatures there is a risk
of gum formation in the first methanation reactor (M1).
Since gum can also be formed due to a high CO concentra-
tion, there is a "double" benefit of using the gas condi-
tioning reactor (GC), because the shift reaction reduces
25 the CO concentration. The amount of steam which is added
upstream of the sulfur guard (SG) is so low that the con-
centration when entering the SG is between 0.01 and 1.00%,
typically 0.3%.

30 The conditioned gas is then passed through two or more
methanation reactors. The embodiment shown in the figure
comprises two methanation reactors (M1 and M2). The heat of

reaction from the methanation reactors is utilized in the boilers (B1 and B2) and the steam superheaters (S1 and S2), and the superheated steam, or at least some of it, is then fed to the turbine (T) driving the recycle compressor (RC).

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In the process of the invention, the steam pressure is preferably 30 bar higher than the feed gas pressure.

From the turbine the used steam is fed to the methanation reactors to lower the potential for carbon formation. The steam is added to the system at a point immediately upstream of the first methanation reactor M1 (where a shift-active catalyst may also be present) after a possible split. This way, none of the added steam will go directly to GC or M2. It would be most efficient to add the steam at a point between the reactors GC and M1. When a shift catalyst and a methanation catalyst both are present, then the two catalysts are advantageously placed in separate reactors, i.e. in GC and M1, respectively. Said separate reactors together operate as an adiabatically operating complex of reactors with the GC reactor placed immediately before M1. Such a complex of reactors is patented by the applicant; see GB 2 018 818 B. If there is no shift-active catalyst present, the steam can be added after the split to the second methanation reactor M2. This option will be more energy efficient. Some of the spent steam from the back pressure turbine may be added to the process stream upstream the desulfurization step.

By using steam this way, at least three surprising advantages are obtained:

1) the carbon equilibrium is moved directly by changing the O/C proportion and the H/C proportion in the reactor,

2) more steam to the turbine driving the compressor gives a higher recycle, which in turn leads to a lower temperature, thereby moving the process conditions away from the carbon region, and

3) the lower temperature gives a higher conversion of synthesis gas to methane in the reactor, because the equilibrium is shifted towards methane at low temperature.

Thus, by first producing high pressure steam and using some of it in a back pressure turbine, which drives the recycle compressor at a relieved pressure, and then adding all the pressure relieved steam or some of it to the process, it becomes possible to minimize the energy consumption and lower the risk of carbon formation compared to a plant where the steam is added directly and the recycle compressor is driven by other means, e.g. electrically.

The invention is illustrated further by means of the following examples.

Example 1

This example compares three different cases, more specifically the traditional SNG process (the first case) and two cases (the second and third case) of the back pressure turbine based process according to the invention. The second and the third case are referred to as "turbine case" and "alternative turbine case", respectively.

In the first case, the traditional SNG process, the steam production is approximately the same as in the two other cases, and the outlet temperature from the first methanation reactor is 675°C. The consumption of electric power to drive the recycle compressor is 1818 kW.

In the second case, feeding additional steam to the gas conditioning reactor increases the distance to carbon formation for the first methanation reactor to 15°C. The outlet temperature from the first methanation reactor is 675°C as in the first case, but the consumption of electric power to drive the recycle compressor is zero.

For the third case (the alternative turbine case) the outlet temperature from the first methanation reactor is increased from 675 to 690°C, while the distance to carbon formation is still 10°C. Again, the consumption of electric power to drive the recycle compressor is zero.

The results are summarized in Table 1 below:

Table 1

	normal case	turbine case	alternative turbine case
steam production, t/h	216.1	211.8	215.1
Electric power consumption, kW	1818	0	0
outlet temp. from 1 st methanation reactor, °C	675	675	690
distance to carbon formation, °C	10	15	10

Example 2

This example illustrates the use of a condensing turbine in the process according to the invention. More specifically, instead of using a back pressure turbine, where effluent steam can be re-used in the process, a condensing turbine is used. The condensing turbine takes the highest possible amount of energy out of the steam, leaving a steam condensate.

Two cases of using a condensing turbine (condensing turbine case and alternative condensing turbine case) have been tested. When compared to the back pressure turbine cases in Example 1, these two condensing turbine cases show that the total steam balance is best for the back pressure turbine embodiment according to the invention.

The results are summarized in Table 2 below:

Table 2

	condensing turbine case	alternative condensing turbine case
steam production, t/h	209.2	205.4
Electric power consumption, kW	0	0
outlet temp. from 1 st methanation reactor, °C	675	675
distance to carbon formation, °C	10	15

The examples clearly show that it is possible at the same time to minimize the energy consumption and lower the risk of carbon formation compared to any plant where the steam

is added directly and the recycle compressor is driven by other means.

Claims:

1. A process for the production of methane and power including the steps of producing syngas from a carbonaceous feed in a manner known *per se* and subjecting the feed syngas (A) to methanation in two or more methanation reactors (M1, M2) after passage through a sulfur guard (SG) for desulfurization, wherein
- 5
- 10 - saturated steam is produced in one or more boilers (B1, B2) and fed to one or more superheaters (S1, S2) to be converted to superheated steam,
- a back pressure turbine (T) is fed with at least some of the superheated steam to drive a recycle compressor (RC) compressing part of the effluent from the last methanation reactor, and
- 15
- all or some of the steam spent in the turbine is added to the methanation process to lower the potential for carbon formation and to save recycle compressor energy.
- 20
2. Process according to claim 1, wherein the heat of reaction from the methanation reactors (M1, M2) is utilized in the boilers (B1, B2) and steam superheaters (S1, S2) to produce superheated steam.
- 25
3. Process according to claim 1 or 2, wherein a higher recycle is obtained by feeding more steam to the turbine (T) driving the recycle compressor (RC).
- 30

4. Process according to claim 3, wherein said higher re-cycle leads to a lower outlet temperature in the first methanation reactor (M1), whereby the process conditions are moved away from the carbon region.

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5. Process according to claim 1 or 2, wherein the syngas feed (A) comprises at least 7 mole% on dry basis of methane.

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6. Process according to claim 5, wherein the syngas feed comprises at least 11 mole% on dry basis of methane.

7. Process according to claim 6, wherein the syngas feed comprises at least 15 mole% on dry basis of methane.

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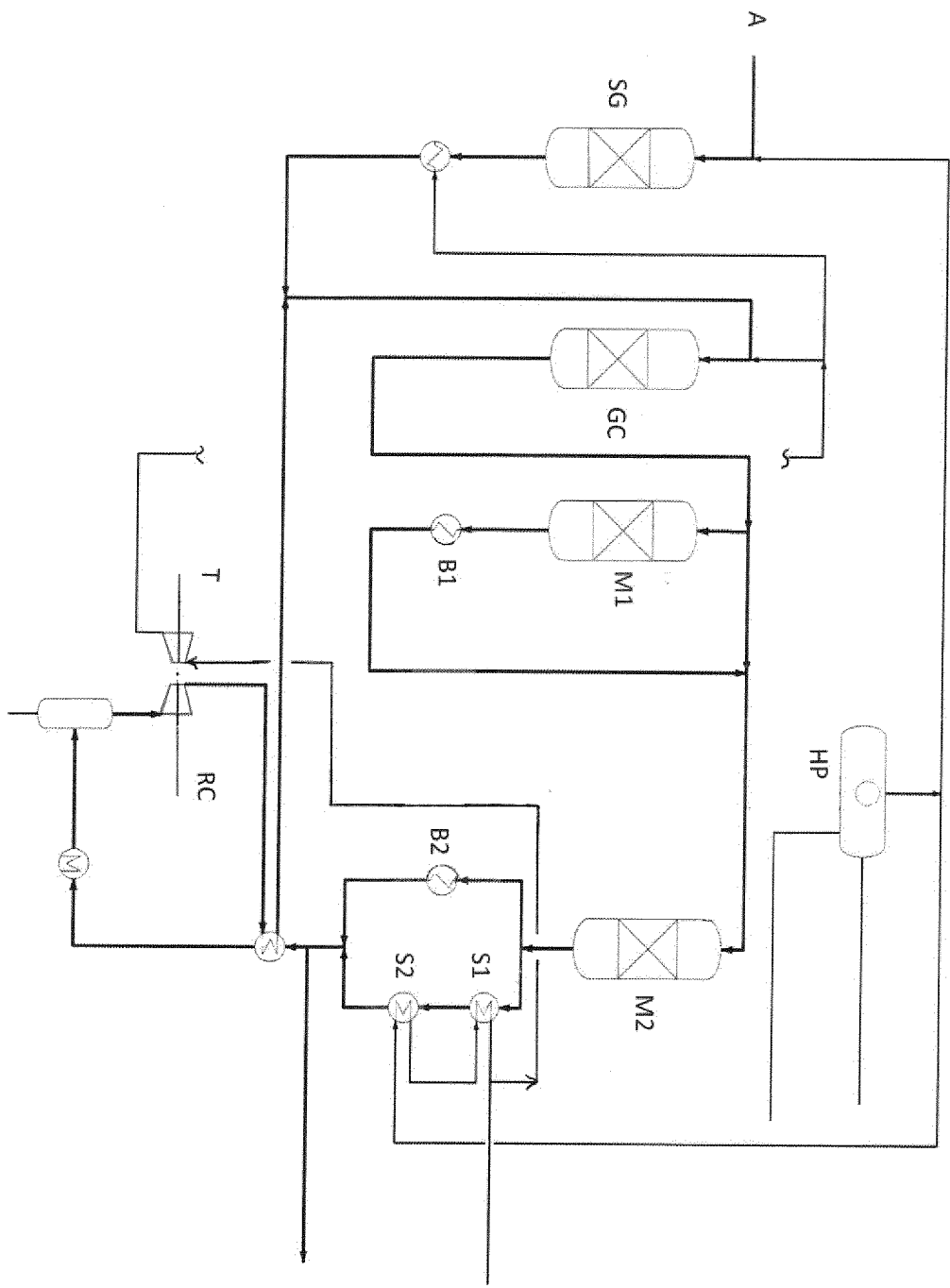
8. Process according to claim 1 or 2, wherein the steam pressure is 30 bar higher than the feed gas pressure.

9. Process according to claim 1 or 2, wherein the steam pressure is 60 bar higher than the feed gas pressure.

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10. Process according to claim 1 or 2, wherein some of the spent steam from the back pressure turbine is added to the process stream upstream the desulfurization step.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/055963

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10L3/08 C10L3/10
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2010/170247 A1 (BOMMAREDDY SAMPATH KUMAR [US] ET AL) 8 July 2010 (2010-07-08) cited in the application paragraphs [0002], [0009], [0021] - paragraph [0030]; claims 7,10-12; figures 1,2 -----	1-10
Y	DE 33 02 260 A1 (COMBUSTION ENG [US]) 10 November 1983 (1983-11-10) claim 1; figure 1 -----	1-10
A	US 2012/093690 A1 (THACKER PRADEEP STANLEY [US]) 19 April 2012 (2012-04-19) paragraphs [0037], [0038]; figure 1 -----	1-10
A	US 2010/286292 A1 (WIX CHRISTIAN [DK]) 11 November 2010 (2010-11-11) paragraphs [0038], [0043], [0046]; figure 3 -----	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

10 May 2016

Date of mailing of the international search report

19/05/2016

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/055963

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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