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(21) International Application Number: PCT/NL99/00256 (22) International Filing Date: 29 April 1999 (29.04.99) (30) Priority Data: 1009038 29 April 1998 (29.04.98) NL (71) Applicant (for all designated States except US): STICHTING ENERGIEONDERZOEK CENTRUM NEDERLAND [NL/NL]; Westerduinweg 3, NL-1755 LE Petten (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): VERINGA, Hubertus, Johannes [NL/NL]; Dorpsstraat 10, NL-1689 EV Zwaag (NL). HEMMES, Katrien [NL/NL]; Graveurstraat 16, NL-1825 EJ Alkmaar (NL). (74) Agent: DE BRUIJN, Leendert, C.; Nederlandsch Octrooibureau, Scheveningseweg 82, P.O. Box 29720, NL-2502 LS The Hague (NL).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> <i>In English translation (filed in Dutch).</i>
(54) Title: METHOD AND APPARATUS FOR THE PRODUCTION OF SYNTHESIS GAS		
(57) Abstract <p>The invention relates to a method and an apparatus for forming synthesis gas from biomass and/or residues. In a biomass gasifier and/or residues gasifier, synthesis gas is formed, part of which is combusted, the combustion heat being transferred to a reformer. In the reformer, a fossil hydrocarbon is converted into synthesis gas which is mixed with the synthesis gas formed in the gasifier. The method and apparatus according to the invention afford a high cold-gas yield, and the production of CO₂ per kilogram of synthesis gas (H₂ and CO) produced is low. Owing to the low degree of integration of the gasifier and the reformer, the H₂/CO ratio can be adjusted over a wide range. The apparatus according to the invention is relatively simple and reliable, given that the only connection between the reformer and the outlet of the gasifier is via a branch line. Coupling the gasifier and the reformer according to the invention permits a gradual transition from the use of fossil fuel to a more sustainable hydrocarbon source. Moreover, the quality of the synthesis gas formed in the biomass gasifier can be improved by mixing with the synthesis gas from the reformer, and control of the feed streams allows a variable syngas composition (H₂/CO ratio) to be achieved.</p>		

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METHOD AND APPARATUS FOR THE PRODUCTION OF SYNTHESIS GAS

The invention relates to a method for forming synthesis gas from hydrocarbons, comprising:

- 5 - feeding a first hydrocarbon and an oxidant to a gasifier and discharging synthesis gas from the gasifier,
- feeding a second, fossil hydrocarbon and steam to a reformer and discharging synthesis gas from the reformer, and
- mixing the synthesis gases formed in the gasifier and in the reformer.

10 The production of synthesis gas from fossil fuels such as coal and natural gas, with the addition of steam and an oxidant such as air, to form hydrogen and carbon monoxide (synthesis gas) is generally known. This steam reforming affords a relatively pure synthesis gas which, because of the shift reaction, also contains CO₂.

German patent application DE-A-3,242,206 discloses an apparatus in which coal in
15 powdered form or a heavy oil fraction are partially oxidized in a gasifier, with the addition of oxygen, at a pressure of between 30 and 100 bar and a temperature of between 1000°C and 1400°C. The hot synthesis gas formed in the process is passed over a water bath to remove soot and slags and is then passed through a tubular reactor in which catalytic steam reforming of LPG takes place at a pressure of between 10 and 40
20 bar and a temperature of between 750°C and 1000°C. The synthesis gases formed in the gasifier and in the reformer are finally mixed in such a ratio that the desired H₂/CO ratio is obtained.

The known apparatus is relatively complex and is not suitable for gasification of biomass and/or residues, whose partial oxidation does not, owing to the relatively high
25 oxygen content naturally present, afford a suitable synthesis gas. Furthermore, when biomass and/or residues are used as a hydrocarbon source for the gasifier, the temperature achieved may be insufficiently high for driving the flow of heat to the reformer. Finally, the known apparatus, in which the reformer is completely integrated with the gasifier, is inflexible with respect to the operating point to be selected of mass
30 streams fed in and the H₂/CO ratio of the synthesis gas formed.

Within the scope of developing sustainable energy sources which involve a reduction in CO₂ emission, and also with a view to the exhaustion of the fossil hydrocarbon sources, gasification of biomass and hydrocarbon-containing residue

streams is of great importance. On the basis of maximum use of the available sources and cultivation in the Netherlands, the estimated extent of the potential use of biomass and residue streams is 165 PJ ($165 \cdot 10^{15}$ J) per year, with a total energy consumption which in the Netherlands today is about 3000 PJ per year. A gradual transition towards a substantial use of sustainable energy is desirable, preference being given to technologies which are able to provide electricity as well as heat and a raw material for the process industry or transport sector, without requiring drastic adjustments to the infrastructure.

Within this scope it is an object of the present invention to provide a method and apparatus for forming synthesis gas from biomass and/or residues, in which a gradual transition of the use of fossil hydrocarbons towards sustainable hydrocarbon sources is possible. It is also an objective of the present invention to provide a method and apparatus in which it is possible for a synthesis gas of relatively high quality to be formed, on an industrial scale, from residues and/or biomass and in which the composition (the H_2/CO ratio) of the synthesis gas can be adjusted over a wide range in a simple manner. It is a further objective of the present invention to form a synthesis gas in an exoenergetically efficient manner, from biomass and/or residues, in which the production of CO_2 per kg of synthesis gas formed is as small as possible.

To this end, the method according to the present invention is characterized in that the first hydrocarbon contains biomass and/or residues and in that part of the synthesis gas discharged from the gasifier is combusted, the heat liberated in the process being supplied to the reformer.

The invention is based on the insight that the heat required for steam reforming is obtained not by combustion of the biomass and/or residues, but by combustion of some of the synthesis gas formed in the gasifier, so that a high cold-gas yield ϕ of the synthesis gas is obtained, based on H_2 and CO ; $\phi = LHV(H_2+CO)_{out}/LHV(biomass + natural\ gas)_{in}$, where LHV is the lower heating value. The avoided fossil CO_2 emission yield, ϕ_{CO_2} , of the process according to the present invention is likewise relatively high:

$\phi_{CO_2} = LHV(H_2+CO)_{out}/LHV(natural\ gas)_{in}$. In other words, the production of CO_2 per kg of $H_2 + CO$ produced is small, and the avoided (fossil) CO_2 emission is therefore large.

Moreover, given the fact that the gasifier and the reformer according to the present invention are not integrated to a large degree, it is possible for the H_2/CO ratio to be adjusted over a wide range. At the same time, a reliable process is obtained, since it is possible, in the event of the supply of biomass and/or residues being interrupted, for the

steam reformer to be operated separately, with the option of feeding the burner of the reformer with natural gas and gas from the gasifier. Finally, the process according to the invention can take place using a relatively simple apparatus, the only measure required being to fit a branch line between the outlet of the gasifier and the reformer.

5 As the gasifier delivers a synthesis gas which is rich in CO and relatively low in hydrogen, whereas steam reforming gives precisely the opposite result, a combination of the two gas streams provides a mixed gas whose composition can be controlled by selecting the ratio between the input of fossil hydrocarbons and biomass. This allows the quality of the syngas of the biomass gasification to be increased and the H₂/CO ratio of
10 the mixed gas to be freely adjusted. The hydrogen/carbon monoxide ratio of the mixed gas is between 0.7 and 5, preferably between 2 and 3. At these values, the mixed gas is suitable for a large number of downstream processes, such as admixture into the gas grid, secondary energy generation, generation of heat and/or power, and production of organic compounds as starting materials for the processing industry.

15 An apparatus in which the method according to the present invention can be implemented advantageously comprises, for example, a gasifier whose bed material is circulated, for the biomass and/or the residues, to which the steam reformer for the fossil hydrocarbon, preferably natural gas, is connected via a branch line.

The invention will be explained in more detail with reference to the appended
20 drawing, in which:

Figure 1 shows a schematic depiction of the combined biomass/residues gasification and hydrocarbon reforming,

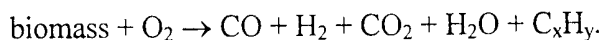
Figure 2 shows a schematic depiction of the syngas composition according to the present invention, and

25 Figures 3 and 4, respectively, show the energy streams and mass streams of a syngas production process according to the present invention.

Figure 1 shows a gasifier 1 with a first inlet 2 for biomass and/or residues, and a second inlet 3 for an oxidant such as, for example, oxygen. The apparatus also comprises a reformer 4 with a first inlet 5 for the supply of fossil hydrocarbons and a steam supply
30 6. The outlet 8 of the gasifier 1 is connected to the reformer 4 by means of a branch line 7. The outlet 8 of the gasifier is further connected to a purification apparatus 10 such as, for example, a scrubber to remove cyclic hydrocarbons and other contaminants such as H₂S, HCl, alkali metals, tarry materials and dust from the syngas. The outlet 9 of the

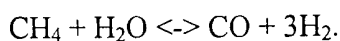
reformer 4 can be connected to the outlet 12 of the purification apparatus 10 to form a mixed gas which can be fed to a CO₂ separator 13. The outlet 14 of the CO₂ separator 13 is connected to a gas separation apparatus 15 for adjusting the composition of the product gas. The gas coming from the gas separation apparatus 15 can be fed to the gas grid, can be used for production of energy, or can, for example, be used as process gas, where CO and H₂ can be reacted together catalytically to produce economically interesting hydrocarbons according to known and proven conversion technologies. It is also possible for the synthesis gas available from the outlet 9 of the reformer 4 to be fed, in its entirety or in part, to the gas grid via line 16. The waste heat of the gases formed at the outlet of the gasifier 1 and the reformer 4 is returned, via heat exchangers 17 and 18, to the gasifier 1 and the reformer 4, respectively. The process in the apparatus according to the present invention is determined by the following reactions:

In the gasifier 1, the reaction taking place is:



The choice of gasification system provides the additional freedom to adjust the relative composition of the gas components. In addition, hydrocarbons (C_xH_y) may form part of the gas components.

In the steam reformer 4, the following reaction takes place, natural gas being fed in via the first inlet 5, steam being supplied via the steam supply 6, and thermal energy being supplied via an internal or external heat exchanger heated by combustion of the synthesis gas coming from the gasifier 1 and supplied via branch lines 7:



In addition, the shift reaction $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$ occurs. Since the gasifier 1 is operated autothermally, CO₂ and H₂O are formed therein. If the oxidant used is ambient air, the synthesis gas at the outlet 8 of the gasifier may also comprise nitrogen. In the reformer 4, CO₂ is formed as a result of the shift reaction taking place to a significant degree. For a number of applications or downstream conversion routes of the process gas, the presence of minor components need not be a disadvantage. If the presence of minor components is not disadvantageous, a relatively coarse removal technique in, for example, purification apparatus 10 may be sufficient. To lower the nitrogen content in the product of the biomass gasifier 1, it would be possible to use pure oxygen, rather than air, in the gasification. In the purification apparatus, the water can likewise be removed in a simple manner from the process gas.

The gasifier 1 and the reformer 4 are operated at temperatures of between 750°C and 1000°C, for example about 800°C-900°C. The gasifier 1 can, for example, be formed by a gasifier having an external burner, such as is manufactured by Manufacturing Technology Conversion International, with a temperature of 850°C and a pressure of 1
5 bar. The reformer 4 comprises a steam reformer known per se having a burner which, for example, is operated at a pressure of 1 bar and a temperature of 1200°C, the pressure in the reformer 4 being 1 bar and the temperature being 815°C. The burner of the reformer is fed with synthesis gas coming from the gasifier.

Figure 2, in the form of a graph, shows how varying the ratio of the quantity of
10 methane fed to the reformer 4 via the inlet 5 and the quantity of biomass fed to the gasifier 1 via the inlet 2 allows the composition of the mixed gas formed after combining the synthesis gases from outlets 9 and 12 to be varied. As the gasifier 1 delivers a synthesis gas which mainly comprises CO, whereas the steam reformer 4 comprises synthesis gas mainly containing H₂, the H₂/CO ratio can be adjusted by selecting the ratio
15 between the input of natural gas and of biomass. In an advantageous embodiment, the H₂/CO ratio is around 2-3 mol/mol. This ratio is particularly beneficial for forming organic compounds, including liquid hydrocarbons.

Figures 3 and 4 respectively show the energy and mass streams of the process according to the present invention for an H₂/CO ratio of 3.16. The figures in brackets
20 give percentages for an energy or mass yield of the synthesis gas formed in total.

Claims

1. Method for forming synthesis gas from hydrocarbons, comprising:
 - feeding a first hydrocarbon and an oxidant to a gasifier and discharging synthesis gas
 - 5 from the gasifier,
 - feeding a second, fossil hydrocarbon and steam to a reformer and discharging synthesis gas from the reformer, and
 - mixing the synthesis gases formed in the gasifier and in the reformer, characterized in that the first hydrocarbon contains biomass and/or residues and in that part of the
 - 10 synthesis gas discharged from the gasifier is combusted, the heat liberated in the process being supplied to the reformer.
2. Method according to Claim 1, characterized in that part of the synthesis discharged from the gasifier is fed to a burner of the reformer.
3. Method according to Claim 1 or 2, characterized in that between 10 and 70
- 15 wt%, preferably between 30 and 50 wt%, of the synthesis gas formed in the gasifier is combusted.
4. Method according to Claim 1, 2 or 3, characterized in that the fossil hydrocarbon comprises natural gas.
5. Method according to Claim 1, 2, 3 or 4, characterized in that the mixing ratio
- 20 of the synthesis gases is set such that the mixing gas has a hydrogen/carbon monoxide ratio of between 0.7 and 5, preferably of between 2 and 3.
6. Method according to any one of the preceding claims, characterized in that the biomass and/or the residues are gasified autothermally.
7. Method according to any one of the preceding claims, characterized in that
- 25 part of the heat generated by combustion of the synthesis gas is used to form steam for the reformer and/or to provide for other heat requirements.
8. Apparatus for forming synthesis gas, comprising a gasifier (1) for biomass and/or residues having a first inlet (2) for the biomass and/or the residues, a second inlet (3) for an oxidant and a first outlet (8) for synthesis gas, a reformer (4) having a first inlet
- 30 (5) for fossil hydrocarbons, a steam supply (6) and a second outlet (9) for synthesis gas, said second outlet (9) being connected to the first outlet (8), and also a branch line (7), connected to the first outlet (8) for feeding part of the synthesis gas formed in the gasifier to a burner which is thermally coupled to the reformer (4).

9. Apparatus according to Claim 8, characterized in that the synthesis gas formed in the gasifier (1) and/or in the reformer (4) is passed via a heat exchanger (17, 18), said heat exchanger being thermally coupled to the gasifier (1) and/or the reformer (4).
- 5 10. Apparatus according to Claim 8 or 9, characterized in that the bed material of the gasifier (1) circulates within the gasification system.
11. Apparatus according to Claim 8, 9 or 10, characterized in that outlet (8) of the gasifier (1) is connected, via a purification apparatus (10), to the outlet (9) of the reformer (4).

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Fig 1

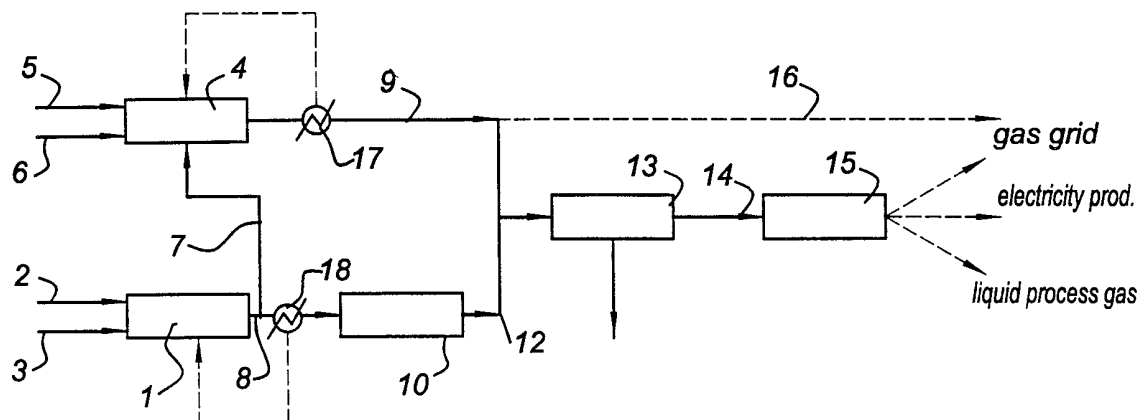
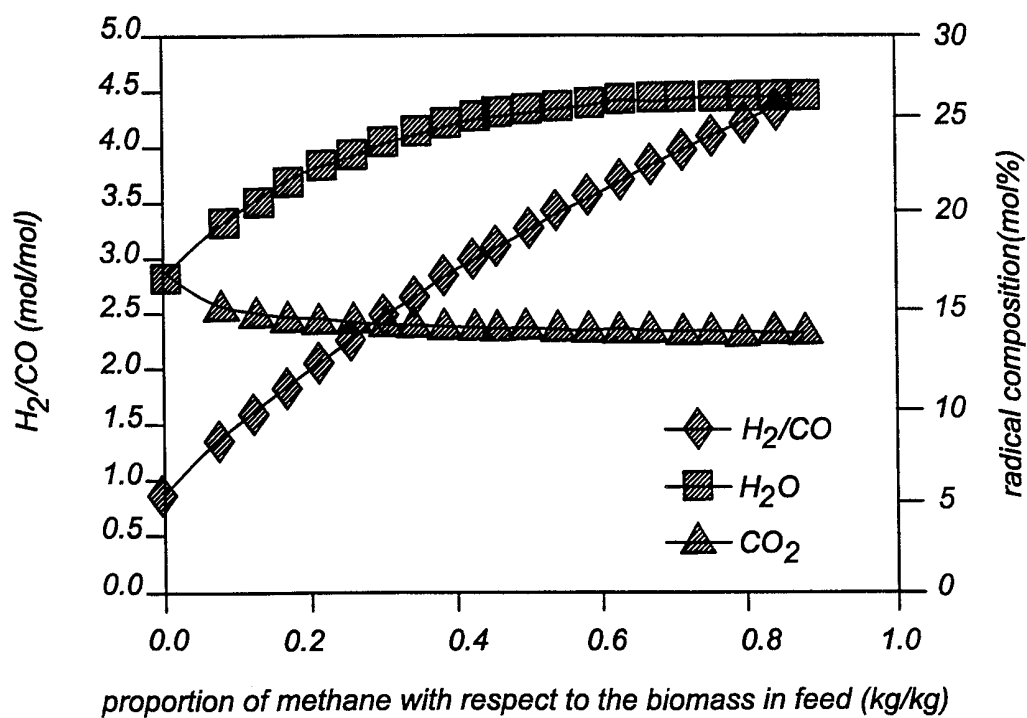


Fig 2

gasification of biomass

reforming of natural gas+
combustion of biomass

2/2

Fig 3

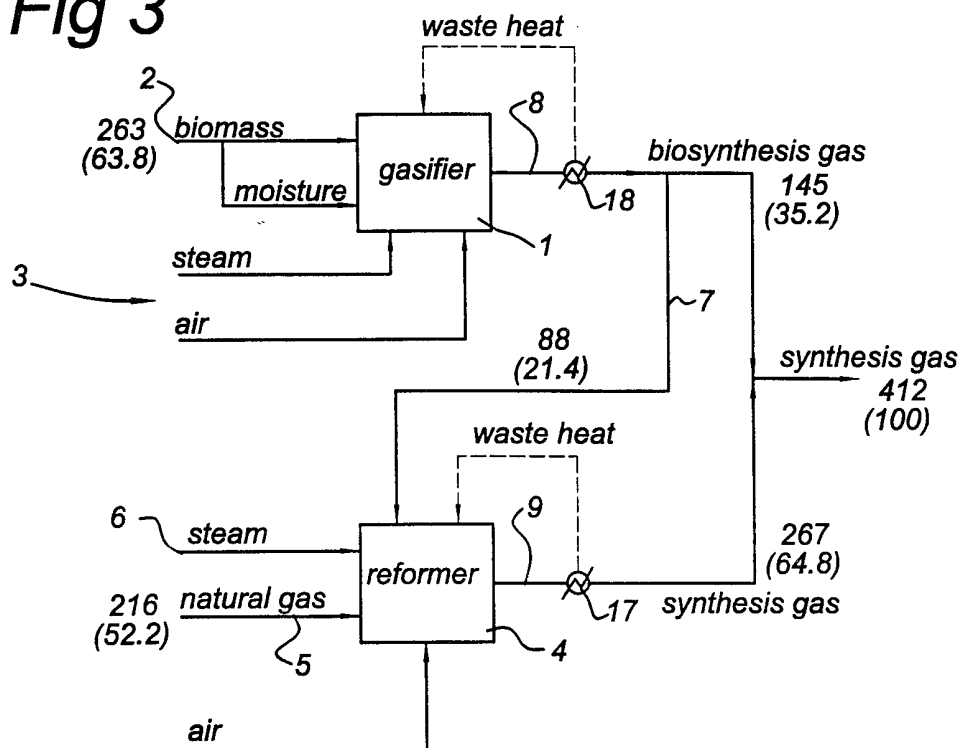
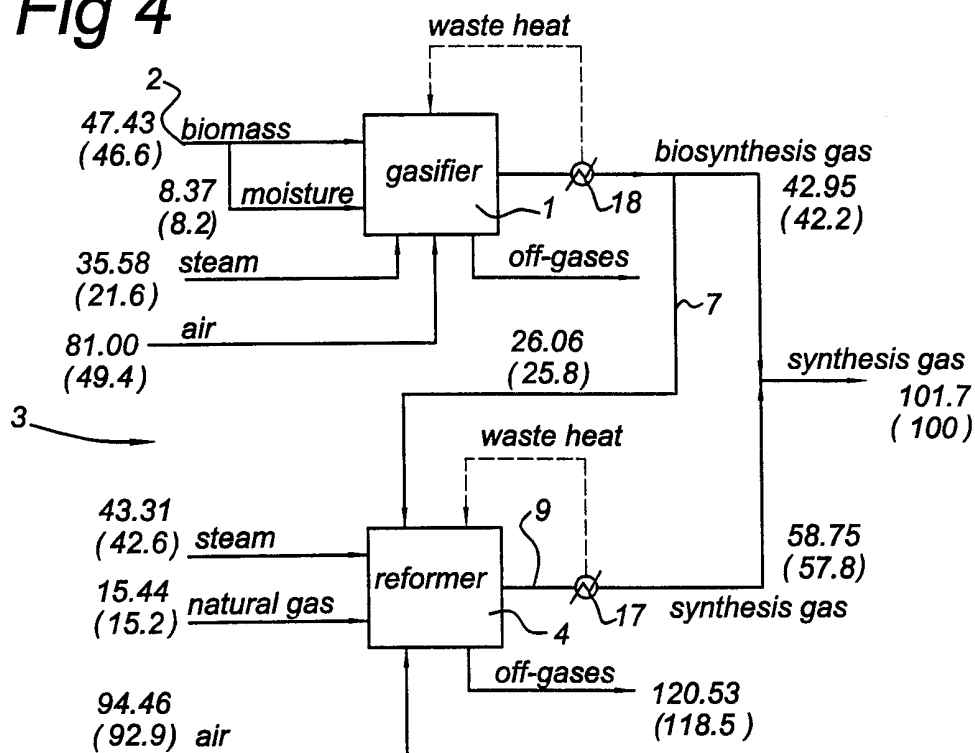


Fig 4



INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 99/00256

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C01B3/38 C01B3/34 C01B3/32 C10J3/54

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)

IPC 6 C01B C10J

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	WALSH J H: "Synthesis of atmospherically-neutral methanol integrated with the generation of electricity in processes equipped for the capture and sequestering of carbon dioxide" 29 March 1993 (1993-03-29) , PROCEEDINGS OF THE INTERNATIONAL ENERGY AGENCY CARBON DIOXIDE DISPOSAL SYMPOSIUM;OXFORD, ENGL MAR 29-31 1993 , ENERGY CONVERS MANAGE;ENERGY CONVERSION AND MANAGEMENT SEP-NOV 1993, PAGE(S) 1031 - 1049 XP002087641 page 1036 - page 1047	1,8

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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