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(54) Title: PROCESS FOR CONVERTING HYDROGEN INTO SUBSTITUTE NATURAL GAS

(57) Abstract

The present invention relates to a process for producing methane–rich product gas (SNG, Synthetic Natural Gas). Biomass and/or fossil fuels, together with hydrogen from an external source, are fed to a hydrogasification reactor. The reaction products from the hydrogasification reactor are converted, in a methanation reactor, into SNG having a Wobbe index of between 40 and 45 MJ/m^3 (s.t.p.), preferably between 42 and 45 MJ/m^3 (s.t.p.), and having a methane molar percentage of at least 75 %, preferably of at least 80 %. The SNG formed can be delivered without any problems to consumers via the existing gas grid and can be used in existing facilities. The process according to the invention can be managed with a compact methanation reactor having a small number of components. In the long term, when the hydrogen from electrolytical processes via sustainable sources will become important, the process according to the invention forms a suitable approach to upgrading biomass and organic waste, using hydrogen, to form SNG. In the short term, however, hydrogen can be obtained from fossil sources.

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Process for converting hydrogen into substitute natural gas

The invention relates to a process for producing methane-rich product gas (SNG, Synthetic Natural Gas), which comprises feeding biomass and/or fossil fuels to a first reactor to form gaseous reaction products and feeding the reaction products from the first reactor to a methanation reactor in which the gaseous reaction product fed thereinto are converted into the methane-rich product gas.

Hydrogen will play an important part in the future sustainable supply of energy. Transportation and storage of hydrogen in its free form (H_2) is more complicated and will probably require much more energy than transportation and storage of hydrogen chemically stored in the form of methane, for example. An additional advantage of the indirect use of hydrogen as a source of energy is that the future (sustainable) supply of energy will still allow use to be made of (parts of) the existing large-scale energy infrastructure such as, for example, the natural-gas grid. One of the possible processes for storing hydrogen in chemically bound form is hydrogasification of carbon-containing compounds such as, for example, biomass and waste. Pyrolysis of these compounds in an H_2 atmosphere allows green natural gas to be produced.

EP-A-0 699 651 discloses that biomass, organic waste or fossil fuels can be converted in a hydrogasification reactor, with the addition of hydrogen, into a gas mixture having a high methane content and with small amounts of carbon dioxide. In a second process step, the gas mixture is converted, in a steam reformer, into synthesis gas which, in a third process step, is converted into methanol in the presence of a catalyst known per se, based on Cu/Zn. The hydrogen remaining at the final step, after removal of the methanol, is passed to the hydrogasification reactor. This process is suitable only for producing methanol.

Also known, from US-A-3,922,148, is a process according to the preamble of Claim 1, where oil is converted, with the addition of steam and oxygen, into synthesis gas which is converted, in a three-stage methanation process, into a product gas containing 99 mol% of methane and 0.8 mol% of hydrogen. Owing to the high CO/CO_2 concentrations of the synthesis gas a relatively large number of methanation reactors are required in order to convert this synthesis gas into methane. In addition, combustion of the oil takes place in the synthesis gas reactor to supply heat in order to form the synthesis gas. Owing to the relatively large heat loss in the methanation reactors, the efficiency of the known process is low.

It is an object of the present invention to provide a process by means of which hydrogen can be stored efficiently and economically in chemically bound form, with relatively little carbon monoxide being present in the synthesis gas formed, and a simple and relatively small methanation reactor being sufficient for the process. To this end, the process according to the invention is characterized in that the first reactor comprises a hydrogasification reactor which is fed with hydrogen, said hydrogen coming from an external source, and in that the product gas (SNG) has a Wobbe index of between 40 and 45 MJ/m^3(s.t.p.), preferably between 42 and 45 MJ/m^3(s.t.p.), and having a methane molar percentage of at least 75%, preferably of at least 80%.

"External" source here refers to a source which is not formed by the methanation reactor, but independently of the process for methane production according to the present invention supplies hydrogen to the hydrogasification reactor, such as hydrogen formed by electrolysis of water, steam reforming of light hydrocarbons, hydrogen formed by partial oxidation of heavy hydrocarbons such as oil or coal by means of steam, or hydrogen from industrial processes such as the production of chlorine by means of membrane or diaphragm cells, methanol production, production of acetone, isopropanol or methyl ethyl ketone, or hydrogen from blast furnaces.

Feeding external hydrogen into the hydrogasification reactor proved to make it possible to obtain a product gas having a Wobbe index, a CH_4 molar percentage and a calorific value which are very close to the Wobbe index, the CH_4 percentage and the calorific value of natural gas (for example Groningen natural gas), so that the SNG formed can be delivered without any problems to consumers via the existing gas grid and can be used in existing facilities. At the same time the process according to the invention can be managed with a very compact methanation reactor having a small number of components, whilst a reduction in the amount of tar formed (compared with other gasification schemes) is also one of the options.

In the long term, where hydrogen from electrolytical processes via sustainable sources will become important, the process according to the invention forms a suitable approach to upgrading biomass and organic waste, using hydrogen, to form SNG. In the short term, however, hydrogen can be obtained from fossil sources. A practical application of this is provided by the following example.

According to an advantageous embodiment of the process according to the present invention, the hydrogen is formed by means of pyrolysis in a plasma reactor, for example via a CB&H process as described in S. Lynum, R. Hildrum, K. Hox, J. Hugdahl: Kvaerner Based Technologies for Environmentally Friendly Energy and Hydrogen Production, Proceedings of the 12th World Hydrogen Energy Conference, vol. I, pp.637-645, 1998. Via the plasma process, hydrogen and pure carbon are formed from natural gas.

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

Fig. 1 shows a schematic depiction of the process to form a methane-rich product gas (SNG) according to the present invention, and

Fig. 2 shows a schematic depiction of a process according to the invention, in which the hydrogen for hydrogasification is obtained from a plasma process.

Fig. 1 schematically shows the process stream for forming substitute natural gas (SNG) according to the invention. Via a feeder 1, biomass is passed to a dryer 2. This biomass can include wood chips, vegetable waste or other organic hydrocarbon sources. As well as biomass it is also possible to feed the hydrogasification apparatus 3 with fossil fuels, a drying step not being required in that case. Via an injection line 4′, CO_2 is introduced into the biomass feed line 4, in order to inject the biomass at the prevailing operating pressure (for example 30 bar) into the hydrogasification apparatus 3. Via a feed line 5, the hydrogasification apparatus is fed with hydrogen from an external hydrogen source. The hydrogen source may comprise a water electrolysis process or be derived from industrial processes in which hydrogen is formed as a by-product.

At the outlet 6 of the hydrogasification apparatus 3, gaseous reaction products are removed from the hydrogasification apparatus, the main constituent being CH_4, with CO, H_2, CO_2 and H_2O also present. The gas mixture is fed, via a heat exchanger 9, to a high-temperature gas purification apparatus 7 to remove solid residue and gaseous impurities from the synthesis gas, for example, H_2S, HCl, HF, NH_3. The solid residue from the hydrogasification apparatus 3 is removed via a discharge line 8. Via line 10 and heat exchanger 11, the purified methane-rich gas mixture is fed to a methanation reactor 12, in which the methane-rich gas mixture is converted into substitute natural gas (SNG) which, via a heat exchanger 14 and a water separator 15, is passed to a discharge line 16. Thence, substitute natural gas can be injected into the existing gas grid to be delivered to the end user.

The heat removed from the methane-rich gas mixture at outlet 6 and in line 10, and the heat removed from the product gas at outlet 13 is supplied, via the heat exchangers 9,11 and 14, to a steam generator 19, the steam generated by which is fed to a steam turbine 20 which drives generator 17 to produce electricity. The condensed steam is recycled from the steam turbine 20 via a return line 22 to the inlet of the steam generator 19. Part of the low-pressure steam from the steam turbine 20 heats the dryer 2 via a heat exchanger 18. The condensed low-pressure steam, having passed the heat exchanger 18, is supplied to the steam generator 19.

The following reactions take place, inter alia, in the hydrogasification apparatus 3:

$$C + 2\,H_2 \leftrightarrow CH_4 \qquad (1)$$

$$CO + 3\,H_2 \leftrightarrow CH_4 + H_2O \qquad (2)$$

$$2\,CO \leftrightarrow C + CO_2 \qquad (3)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (4)$$

At a constant temperature (T=800°C), if no hydrogen were to be fed in at thermodynamic equilibrium, a pressure increase in the reactor would lead to:

- a decrease in the CO and H_2 concentration and an increase in the concentrations of CH_4, CO_2 and H_2O in the synthesis gas discharged via the discharge line 6;
- a decrease in the conversion of carbon from the biomass, and
- a decrease in the heat required in the reactor 3.

The abovementioned reaction number (4), the water gas shift equilibrium, is independent of the pressure, whereas the other reactions are shifted to the right with increasing pressure and are all exothermal in that direction.

At higher operating temperatures, at a pressure P=30 bar, if no hydrogen is fed in and at thermodynamic equilibrium, the above mentioned four equilibrium reactions are shifted to the left, which results in:

- an increase in the CO and H_2 concentration and a decrease in the concentrations of CH_4, CO_2 and H_2O in the synthesis gas discharged via the discharge line 6;
- an increase in the conversion of carbon from the biomass, and
- an increase in the heat demand of the reactor.

Only at temperatures below 550°C will the process become autothermal.

Feeding in hydrogen at T=800°C, P=30 bar and at thermodynamic equilibrium gives rise to the following effects in the hydrogasification process in the hydrogasification apparatus 3:

- an increase in the methane concentration and a decrease in the heat demand according to reactions (1) and (2),
- a decrease of the CO concentration according to reaction (2), and
- an increase in the carbon conversion according to reaction (1).

If hydrogen is fed in via the feed line 5 to an amount of 75 mol/kg of biomass (moisture-free), the synthesis gas formed in the hydrogasification apparatus 3 comprises 29 vol% of methane and 7 vol% of CO, with a carbon conversion of the biomass of 78% and a heat demand of 1.2 MW_{th}/kg of biomass (moisture-free). Wherever biomass is referred to hereinafter, this relates to moisture-free biomass. An increase in the operating pressure T=800°C, with a hydrogen feed of 75 mol/kg of biomass, will result in an increase in the carbon conversion, since reaction (1) becomes dominant in that case.

There follows a more detailed description of the process parameters in the hydrogasification apparatus 3, the high-temperature gas purification apparatus

7, and the methanation reactor 12, these parameters having formed the basis for calculating the composition of the substitute natural gas (SNG) discharged via the discharge line 16. The calculation was based on biomass in the form of poplar sawdust having the composition as shown in Table 1:

Table 1 Specification of the biomass (Poplar sawdust)

		Units	Value
Composition	C	wt%	51.32
	H	wt%	6.16
	N	wt%	1.18
	S	wt%	0.13
	O	wt%	34.57
	Ash	wt%	6.64
	Total	wt%	100.00
Low heating value $(LHV)_{moisture\text{-}free}$		MJ/kg	21.57
Low heating value (LHV), 30 wt% moisture		MJ/kg	14.53

In the computational model, the hydrogasification apparatus 3 was operated at a temperature of 800°C and a pressure of 30 bar. At this setting it is possible, given a specific deviation from the thermodynamic equilibrium, to obtain a carbon conversion of the biomass of 89%, with a hydrogen feed of 75 mol/kg of biomass, the process being autothermal. Since, however, the biomass fed in is not free from moisture, and the hydrogasification apparatus 3 is fed with additional CO_2, the hydrogen feed in the model was increased from 75 to 100 mol/kg of biomass to render the process autothermal. At this setting, the predicted conversion of carbon from the biomass is 83%.

The gaseous products from the hydrogasification reactor 3 are cooled in two steps, via heat exchangers 9 and 11, from 850°C to the inlet temperature of the first methanation reactor at 400°C. In this temperature range, a high-temperature gas purification apparatus 7 can be used to remove solid residue and gaseous contaminants such as H_2S, HCl, HF, NH_3 from the synthesis gas.

The methanation reactor 12 is based on the ICI high-temperature single-pass process as described in the Catalyst Handbook, second Edition, edited by M.V. Twigg, ISBN 1874545359, 1996. This makes use of a series of reactors operating at successively lower outlet temperatures.

The steam generator 19 generates superheated steam at a pressure of 40 bar. The heat derived from the methanation reactor 12 and from the cooling of the methane-rich synthesis gas via heat exchangers 9 and 11 was used in the model to form steam, while the remainder of the heat released during cooling of the methane-rich gas mixture in lines 6 and 10 was used to superheat steam. The steam formed was expanded to 0.038 bar in two steps (from 40 to 10 bar in the first step, and from 10 to 0.038 bar in the second step).

Based on the abovementioned process settings, the mass balance and energy balance of the system according to Figure 1 were calculated using the ASPEN PLUS process simulation program. Table 2 shows the properties of Groningen natural gas (NG) and of the synthetic natural gas (SNG) formed in the hydrogasification process according to Figure 1. Very importantly, it can be seen that the heating value in MJ/kg and the Wobbe index of the synthetic natural gas are virtually identical to those of natural gas. This allows the product gas formed in the hydrogasification process according to Figure 1 to be injected directly into the natural-gas grid and to be burnt using existing facilities.

Table 2 Properties of the product gas (SNG) and Groningen natural gas (NG)

Composition		NG	SNG
CH_4	mol%	81.30	81.55
H_2	mol%	0.00	8.70
CO_2	mol%	0.89	8.54
C2+	mol%	3.49	<1
N_2	mol%	14.31	0.77
0_2	mol%	0.01	0.00
Molecular weight	kg/kmol	18.64	17.33
Low heating value (LHV)	MJ/kg	38.00	39.00
Low heating value (LHV)	MJ/kmol	708.32	676.08
Wobbe index	MJ/m^3(s.t.p.)	44.20	43.87

The Wobbe index, based on cubic meters at standard temperature and pressure (m^3[s.t.p.]) at 0°C and 1 atmosphere (MJ/m^3[S.T.P]), is the ratio of the high calorific value and the square root of the relative density of the gas. The Wobbe index is defined according to the following formula:

$$W = \frac{HHV}{\sqrt{(\rho_g / \rho_{air})}}$$

where HHV is the high heating value in MJ/m^3(s.t.p.), and ρ_g and ρ_{air} are the densities of gas and air, respectively, in kg/m^3(s.t.p.). The Wobbe index is the measure of the amount of energy which is delivered to a burner via an injection.

Two gases having a different composition but the same Wobbe index provide the same amount of energy, given a predetermined injection direction at the same injection pressure.

Figure 2 shows an embodiment of a process in accordance with the present arrangement, in which the hydrogen is formed via a CB&H process as described in R.A. Wijbrans, J.M. van Zutphen, D.H. Recter: "Adding New Hydrogen to the Existing Gas Infrastructure in the Netherlands, Using the Carbon Black & Hydrogen Process, Proceedings of the 12th World Hydrogen Energy Conference", vol. II, pp. 963-968, 1998. Here, natural gas is fed, via a feed line 23, to a plasma reactor 24 in which a plasma is generated by electrical energy being supplied, and in which hydrogen and carbon are formed. Having passed a heat exchanger 25 and a separator 26, the carbon in the known CB&H process is discharged to be pelleted and packaged and the hydrogen is passed to a compression and injection apparatus 27 in order then to be injected into the natural-gas grid. According to the invention, the hydrogen is passed not to compression and injection apparatus 27, but to the hydrogasification process, via the feed line 5. The use of the high-temperature plasma process to produce hydrogen from natural gas in combination with the hydrogasification process has the advantage that the CB&H process yields pure carbon, the reduction in calorific value as a result of the conversion of natural gas into hydrogen being compensated for, by more than 100%, by back-reaction of the hydrogen to form SNG. This therefore ensures that the fossil carbon disappears from the chain, whereas sustainable carbon is fed from the biomass, with a net gain in energy, owing to the introduction of biomass to an amount of roughly 60%.

CLAIMS

1. Process for producing methane-rich product gas (SNG, Synthetic Natural Gas), which comprises feeding biomass and/or fossil fuels to a first reactor to form gaseous reaction products and feeding the reaction products from the first reactor to a methanation reactor in which the gaseous reaction product fed thereinto are converted into the methane-rich product gas, characterized in that the first reactor comprises a hydrogasification reactor which is fed with hydrogen, said hydrogen coming from an external source, and in that the product gas (SNG) has a Wobbe-index of between 40 and 45 MJ/m^3 (s.t.p.), preferably between 42 and 45 MJ/m^3 (s.t.p.), and having a methane molar percentage of at least 75%, preferably of at least 80%.

2. Process according to Claim 1, characterized in that the product gas (SNG) has a calorific value which matches the calorific value of natural gas.

3. Process according to Claim 1 or 2, characterized in that the product gas is injected into a natural-gas pipeline system and is delivered to consumers.

4, Process according to Claim 1, 2 or 3, characterized in that the hydrogasification reactor is operated at a temperature of between 500°C and 1500°C, preferably between 750°C and 850°C, at a pressure of between 15 bar and 200 bar, preferably between 20 bar and 40 bar.

5. Process according to Claim 4, characterized in that CO_2 is introduced as a carrier gas into the biomass or the fossil fuels to inject these into the hydrogasification reactor.

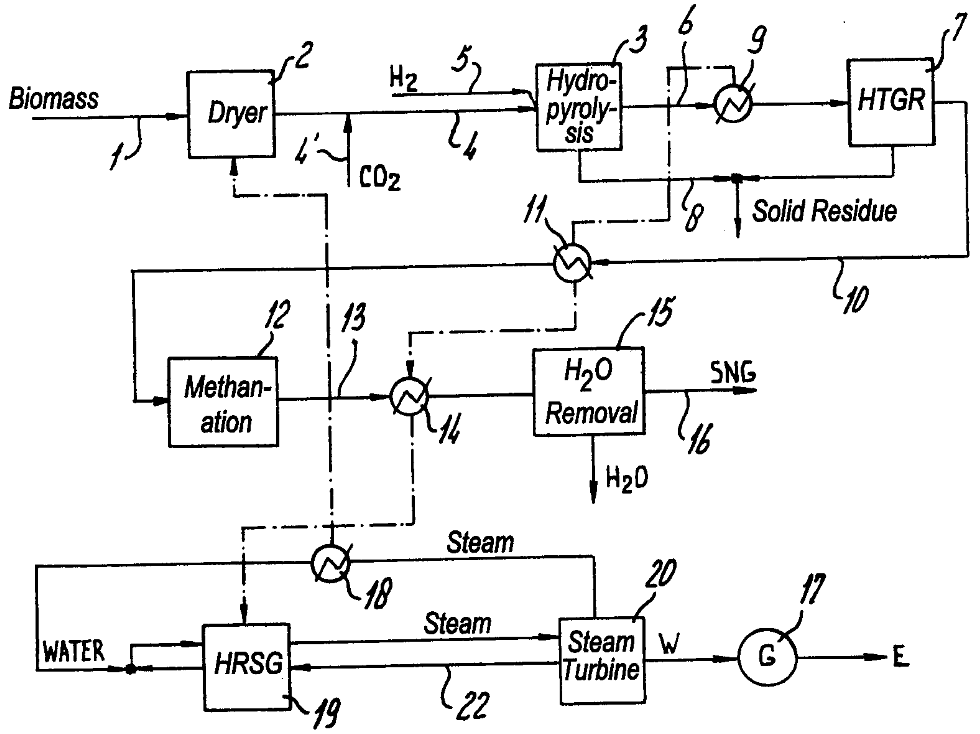
6. Method according to any one of Claims 1 to 5 inclusive, characterized in that the amount of hydrogen fed to the hydrogasification reactor is controlled in such a way that the hydrogasification in the hydrogasification reactor proceeds at least virtually autothermally.

7. Method according to Claim 6, characterized in that the hydrogasification reactor is fed with between 50 and 125 mol of hydrogen per kg of moisture-free biomass.

8. Method according to any one of the further claims, characterized in that the heat produced in the methanation reactor is supplied to a steam generator.

9. Method according to any one of the further claims, characterized in that the hydrogen is formed from natural gas by means of pyrolysis in a plasma reactor.

fig-1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H2
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Hydro-pyroly-sis
3
6
9
HTGR
7
8
Solid Residue
11
10
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15
Methan-ation
14
H2O Removal
SNG
16
H2O
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WATER
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Steam
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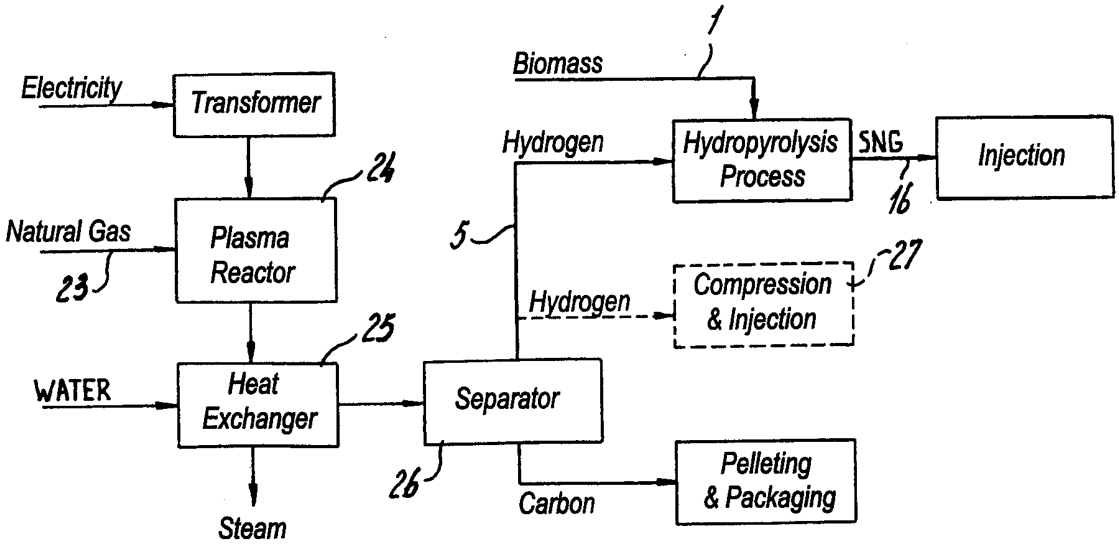
fig-2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Transformer
24
Natural Gas
23
Plasma Reactor
25
WATER
Heat Exchanger
Steam
Biomass
1
Hydrogen
Hydropyrolysis Process
SNG
16
Injection
5
Hydrogen
Compression & Injection
27
Separator
26
Carbon
Pelleting & Packaging

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/NL 99/00630

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C1/04 C10K3/04 C10L3/08

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 7 C07C C10L C10K

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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A	US 3 993 457 A (CAHN ROBERT P ET AL) 23 November 1976 (1976-11-23) claims 1,5-8 column 4, line 55 - line 63 ---	1
A	US 3 967 936 A (SCHORA JR FRANK C ET AL) 6 July 1976 (1976-07-06) claim 1 column 2, line 59 - line 64 ---	1
A	FR 2 593 493 A (BRITISH PETROLEUM CO) 31 July 1987 (1987-07-31) claim 1 --- -/--	1,9

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

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search 10 January 2000	Date of mailing of the international search report 20/01/2000
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INTERNATIONAL SEARCH REPORT

Inte   onal Application No
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C.(Continuation) 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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1

INTERNATIONAL SEARCH REPORT

Information on patent family members

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