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(54) Title: METHOD FOR THE PREPARATION OF DIMETHYL ETHER

(57) Abstract

The invention relates to a method for the preparation of dimethyl ether from synthesis gas of an HCR value of at least 1.4, comprising: converting the synthesis gas in a reactor at least partly into a reaction mixture containing dimethyl ether, methanol and water; cooling the reaction mixture, thereby forming a first liquid phase containing methanol, dimethyl ether and water, and a first gas phase containing unconverted synthesis gas, CO_2, dymethyl ether, methanol and water; washing the first gas phase with a washing liquid substantially containing methanol, thereby forming a second gas phase substantially containing H_2, CO and CO_2, and a second liquid phase substantially containing methanol, dimethyl ether, water and CO_2; recovering CO_2 from the first and the second liquid phase and recirculating this CO_2 together with the second gas phase to the reactor, and recovering dimethyl ether from the first and the second liquid phase.

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Title: Method for the preparation of dimethyl ether

This invention relates to a method for the preparation of dimethyl ether (DME; CH_3-O-CH_3).

Prompted by an increasing concern about the air quality in urban areas, there has been a longtime search for a good alternative for vehicles that use diesel as fuel. Fuels such as natural gas, LPG and methanol are suitable alternatives in terms of emissions, but they suffer from the disadvantage that the energy consumption of the vehicle increases by 20 to 30%. The reason for this is that these fuels are used in Otto engines, which have a lower efficiency compared with diesel engines.

Recently, however, it has been found that DME combines low emissions with the low energy consumption characteristic of diesel engines. DME can be produced from different raw materials. In addition to natural gas, coal and oil, renewable sources such as biogas, biomass and various vegetable raw materials can be used for the production. To enable DME production, it is necessary first to produce synthesis gas, in which important components are hydrogen and CO.

Synthesis gas is characterized *inter alia* by the so-called H_2/C ratio, that is, the molar ratio between hydrogen and carbon monoxide. In the presence of water, however, the water-gas shift reaction occurs in the syngas. This reaction is an equilibrium reaction and is dependent on the prevailing conditions. The equation for this reaction is as follows:

$$CO + H_2O <=> CO_2 + H_2$$

As a result of this reaction, the H_2/CO ratio changes. For the syngas to be still typed properly, independently of the presence, if any, of water in the mixture and the position of the water-gas equilibrium, the

H_2/C ratio is so defined as to be independent of the position of the water-gas equilibrium.

$$\text{HCR value} = \{ [H_2] - [CO_2] \} / \{ [CO] + [CO_2] \}$$

DME is gaseous under atmospheric conditions and liquefies at a pressure of about 5 bar. For that reason, similarly to LPG, it can be stored in liquid form in the fuel tank of the vehicle. The energy density (MJ/liter) of liquid DME is approximately half that of diesel. This implies that twice as much fuel has to be carried along for the same range. Another consequence is that also twice as much fuel must be injected to produce the same amount of engine power.

Combustion engines on DME have a clearly lower emission of NO_x and particles than do diesel engines. In terms of the CO_2 emissions for the entire route from source to wheel, DME compares well with other fuels. When DME is produced from renewable raw materials, the CO_2 emission will even be significantly lower than in fuels produced from fossil sources. Also, when DME can be produced on site on a small scale, a large part of the CO_2 emission for recovery and transport is eliminated.

Currently, DME is mainly used as a propellant in replacement of noxious CFCs. The worldwide synthesis capacity of DME is estimated at 150,000 tons/year. For comparison, the demand for methanol for various applications is estimated, for 1997, at 25.5 million tons. For this application, DME is produced by dehydration of methanol in a separate reactor or as a by-product during the methanol synthesis itself. The thus-produced DME is comparatively expensive, which renders it unsuitable to be used as fuel on a large scale.

Research has already been carried out on methods for producing so-called fuel-quality DME. In German patent application 42 22 655, a method is disclosed in which DME is prepared from synthesis gas having an H_2/C ratio of about 1. In this method, the synthesis gas is supplied at a pressure of about 60 bar to a reactor filled with a combination of a methanol preparation catalyst and a dehydration catalyst. In this reactor, first methanol is formed, which is subsequently converted to DME. Since the conversion occurs only partly, the reaction mixture, which, in addition to unconverted synthesis gas and DME, also contains a quantity of methanol, CO_2 and water, requires further processing. According to this method, the reaction mixture is first cooled, yielding a liquid phase consisting substantially of methanol and DME, with some water, inert, and a part of the CO_2. The residual gas phase contains substantially H_2, CO and CO_2, as well as smaller amounts of DME, methanol and inert.

The gas is washed with methanol to remove DME and CO_2. The residual gas phase is substantially recirculated to the reactor. The washing liquid, which contains the greater part of the CO_2, is desorbed, whereafter the methanol is recirculated to the washing column. The gas phase of the desorption is washed in a second washing column, to recover residues of methanol and DME, whereafter CO_2, containing traces of DME, is discharged.

The liquid phase obtained upon cooling of the reaction mixture is also supplied to the second washing column. From the bottom of this column, a mixture of DME, water and methanol, of varying composition, is obtained.

In this method, the conversion of the synthesis gas is controlled such that, in addition to DME and methanol, CO_2 is formed as a residual product.

Another method is described in WO-A96/23755, in which the method is controlled such that, as residual product, water is formed, while CO_2 is recycled.

In this method, the starting point is an H_2/C ratio in the synthesis gas of about 2, while, to obtain a sufficient yield, a comparatively poor purity is accepted.

This method is characterized, *inter alia*, in that the gas phase obtained after cooling of the reaction mixture is for the greater part recirculated over the reactor. The rest of the gas phase is subsequently washed with methanol derived from the process, which washing liquid is dehydrated in a second reactor, thereby forming DME. The top product is discharged. From the liquid phase of the reaction mixture, gaseous DME is recovered in a distilling column. The bottom product, substantially consisting of water and methanol, is subsequently separated in a distilling column into a liquid residual stream substantially consisting of water and inert, and gaseous methanol which, after cooling, is used as washing liquid.

Although this method does not have the disadvantage of the formation of large quantities of CO_2 that are discharged, it is still far from ideal. As already indicated, a low purity of the DME (<70%) is accepted. Also, two separate reactors are needed, and their volume is very large owing to the large recycle of DME over the reactor.

The object of the invention is to provide a method for the preparation of DME, in which these disadvantages of the prior art do not occur. More particularly, the object of the invention is to provide a method in which the reaction yields water as a by-product, so that no CO_2 is produced, or just minor quantities of CO_2 are produced.

A further object of the invention is to provide a method by which DME can be produced in a sufficient (>85%) purity. It is also an object of the invention to keep the method as simple as possible, which means, *inter alia*, that it is not necessary to have the conversion take place in different reactors.

The invention relates to a method for the preparation of dimethyl ether from synthesis gas having an HCR ratio of at least 1.4, comprising

- converting the synthesis gas in a reactor at least partly into a reaction mixture containing dimethyl ether, methanol and water,

- cooling the reaction mixture, thereby forming a first liquid phase containing methanol, dimethyl ether and water, and a first gas phase containing unconverted synthesis gas, CO_2, dimethyl ether, methanol and water,
- washing the first gas phase with methanol, thereby forming a second gas phase containing substantially H_2, CO and CO_2, and a second liquid phase containing substantially methanol, dimethyl ether, water and CO_2,
- recovering CO_2 from the first and the second liquid phase and recirculating this CO_2, together with the second gas phase, to the reactor, and
- recovering dimethyl ether from the first and the second liquid phase.

Surprisingly, it has been found that in this way dimethyl ether can be prepared in a high purity. The thus-obtained dimethyl ether is suitable for use as fuel, in replacement of diesel, but may also be further purified.

Characteristic aspects of this process are the separation of the product stream after the reactor by cooling and separation of a liquid phase combined with washing of the residual gas phase with a washing liquid which preferably contains substantially methanol, and recovering and recycling to the reactor CO_2 extracted from the gas phase into the liquid phases.

By these measures, *inter alia*, it is possible to combine good process control with a high purity, while maintaining a simple process. Also, this method enables good reactor utilization. The process is suitable for the production of DME from synthesis gas of an HCR of 1.4 or more, preferably at least 2. DME can be produced with different HCR values. At HCR <1.4, more CO_2 than H_2O is formed as waste product. At HCR >1.4, more water is formed. At HCR >= 2, it is possible to run the process without removing CO_2 from the process. In that case, only DME and water are formed, although in different discharges and along with the discharged water, relatively small quantities of carbon and hydrogen compounds are discharged (in any case H_2, CO, CO_2 and methanol); the exact amounts of these losses and the exact composition of the product are in equilibrium with the HCR of the synthesis gas used.

According to a preferred embodiment of the method according to the invention, the first liquid phase is further separated in a column into a third liquid phase containing methanol and dimethyl ether, and one or more liquid phases and gas phases. In this column, preferably at least one additional liquid phase is formed, containing substantially water. This is discharged as residual product, optionally after further cleaning. This stream also contains liquid inert components, which are discharged from the system in this manner.

According to a further elaboration of the invention, from the last-mentioned column, a fourth liquid phase containing methanol is obtained, which is preferably recirculated to the reactor. This methanol stream is tapped from one of the plates of the distilling column. If necessary after evaporation, it is then combined with the recirculating synthesis gas. This embodiment has the advantage that already at the inlet of the reactor a quantity of methanol is present, so that, accordingly, dimethyl ether can be formed from the beginning. Also, the recycle of methanol, an intermediate for the formation of DME, increases the total conversion, on a carbon basis, of the process.

Further variants and preferred embodiments of the invention will be further explained in and by the description of the drawings to be given hereinbelow.

The method according to the invention starts from synthesis gas, that is, a gas containing H_2, CO and possibly CO_2. In view of the objective of the invention to limit the residual products to water as much as possible, and to permit only a minimal emission of CO_2, it is essential that the HCR value in the synthesis gas is at least 1.4, preferably at least 2.0. In practice, it has been found that at such a ratio in the initial gas, as a result of the recycle and the consumption, eventually a state of equilibrium will be established, while this ratio is considerably higher in the reactor.

Synthesis gas can be prepared from practically all hydrocarbon-containing raw materials. The preparative processes vary greatly for different raw materials. To be mentioned are, for instance, (sub)processes such as coal gasification or fermentation of biomass. When the raw material is natural gas, synthesis gas can be prepared, *inter alia*, by steam reforming:

$$CH_4 + H_2O \Rightarrow CO + 3H_2 \qquad HCR = 3$$

In addition, much research is currently being performed on partial oxidation:

$$2CH_4 + O_2 \Rightarrow CO + 2H_2. \qquad HCR = 2$$

The skilled person, on the basis of what is known about the preparation of synthesis gas, will be able to set the HCR value. This can be done, as already indicated hereinabove, by forming a combination of both steam reforming and partial oxidation of natural gas, such as autothermal reforming or combined reforming. Examples of this kind of processes are the Gas Heated Reforming (GHR) of ICI and Kellogs' Reformer Exchanging System (KRES).

The reactor for the preparation of the dimethyl ether is preferably a fixed bed reactor, more particularly a cooled tubular reactor, having therein a combination of two catalysts, viz. a methanol preparation catalyst and a dehydration catalyst. These catalysts can be used as a mixture or in layers. It is preferred to use a mixture.

Suitable catalysts for this reaction are known and commercially available. Examples of methanol preparation catalysts are CuO and ZnO. Eligible as dehydration catalysts are, for instance, catalysts based on γ-Al_2O_3.

In the reactor, the following equilibrium reactions occur.

$$CO + 2H_2 \rightarrow CH_3OH$$

$$2\ CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

The overall reaction is then

$$2CO + 4H_2 \rightarrow CH_3OCH_3 + H_2O$$

This will make it clear that the H_2/C ratio (HCR) must be at least 2. During the reaction, also CO_2 may be formed, according to the equilibrium reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

By the recycle of CO_2, however, this reaction is as good as suppressed. To remove gaseous inert components which always enter the system via the synthesis gas or are formed as by-product during the reactions, a part of the gas will have to be discharged from the system. From the combination of conversions and the nature and amount of the discharge, it can then be derived what HCR value must be used in the synthesis gas.

The reaction occurs at elevated temperature and pressure, which are not very critical. The pressure is generally between 10 and 100 bar, with a preferred range of between 25 and 75 bar. In general, it will be endeavored to keep the pressure in the system at the same level as much as possible, since this saves compression costs. It has been found, however, that the separation of CO_2 from DME at pressures above about 57.5 bar is difficult. The temperature is preferably between 175 and 350°C, with a particular preference for the range of 200 to 330°C. The maximum temperature is mainly dictated by the limited temperature resistance of the catalyst. Thus, as a consequence of the temperature profile in the reactor, at the same time the temperature range in which the reaction proceeds is defined.

The invention is presently further elucidated with reference to the drawing representing a flow diagram of a possible embodiment of the method according to the invention. To illustrate the method according to the invention, a possible mode of the process is illustrated with reference to a flowsheet.

Synthesis gas, after combination with a number of streams to be indicated hereinafter, is supplied via line 1 to reactor 2. In this reactor, *inter alia* dimethyl ether is formed. The reaction mixture, after cooling (not drawn), is supplied via line 3 to separator 4. Via line 5, the first liquid phase is supplied to distilling column 6. The bottom product, substantially comprising water, is discharged via line 7.

The gas phase obtained in separator 4 is supplied via line 8 to washing column 9, where the gas is washed with methanol derived from distillation step 10 via line 23. The residual gas phase, substantially H_2 and CO_2, is recirculated via line 11 and line 1 to the reactor 2.

The liquid phase derived from the washing column is passed via line 12 to the distillation step 10. To this distillation step 10, which may consist of one or more distilling columns, there are also supplied, via lines 13 and 14, the gas phase and the liquid phase derived from the distilling column 6. A liquid phase substantially comprising methanol is discharged from distilling column 6 via line 15 and recirculated via line 1 to the reactor 2.

A gas phase, substantially containing CO_2, is recirculated via line 16 and line 1 to the reactor 2. Via line 17, finally, dimethyl ether is discharged. Depending on the desired purity and the intended use, the dimethyl ether can be further purified.

Fig. 2 gives a possible elaboration of the distillation step 10.

To distilling column 18 there are supplied via lines 12 and 13, respectively, a liquid and a gas phase, coming from washing column 9 and distilling column 6, respectively. From the bottom of the column, a stream substantially comprising methanol is obtained, which is passed via line 23 to the washing column 9.

The gas phase, CO_2, is discharged via line 21 and recycled to the reactor via line 16. Via line 20 a liquid is supplied to distilling column 19. From the bottom of the column, the product dimethyl ether is obtained, and at the top CO_2 is removed, which is combined via line 22 with the CO_2 in line 16.

Starting from the above-described flow diagram, the process can be carried out as follows. Synthesis gas is supplied to the process via line 1. This synthesis gas is united with the recycle stream in lines 11, 15 and 16. After compression and heating, the stream is passed through the reactor where DME and methanol are formed, and cooled again. In the separator 4, the cooled stream is further cooled and a liquid phase is separated, containing mainly water, methanol and DME. The residual gas phase substantially containing H_2, CO, CO_2 and DME is passed to the washing column 9 where the greater part of the DME is washed out, using the washing liquid in line 23 substantially comprising methanol. A large part of the CO_2 from the gas stream 8 is washed out along with the methanol.

The separated liquid phase is separated in the distilling column 6 into

a) a stream 7, which mainly comprises water, and is discharged

b) a stream 14, which contains as much as possible of the DME from 5

c) a gas phase 13, which contains volatile components, including H_2, CO and CO_2, which can be recycled

d) a liquid stream 15, which is tapped from a plate, contains substantially methanol and is recycled to the reactor via the stream 15 briefly explained hereinbelow.

The liquid stream 12 from the wash column, which includes the DME and CO_2, is mixed with the methanol- and DME-containing stream 14. This combined stream is heated and supplied to the distilling column 18. In 18, the following streams are separated:

a) 23, which mainly contains the original washing liquid.

b) .20, which contains the "crude" DME, some methanol and an amount of CO_2.

c) 21, which in turn contains a residue of volatile gases.

The crude DME 20 is separated in the distilling column 19 into:

a) the product stream "DME", which contains approximately 91% pure DME.

b) as much as possible of the CO_2 dissolved in the DME, in the stream 22.

All separated CO_2 streams are joined in the stream 14. Together with the methanol in stream 15, these intermediates are recirculated to the reactor.

Further, in the process, discharge streams are tapped at two points. From the gas phase stream which is recycled, a discharge stream is tapped after the washing column. Likewise, a discharge stream is tapped from the methanol washing stream, so that no water accumulation occurs in the washing liquid.

EXAMPLE

On the basis of the method according to Figs. 1 and 2, dimethyl ether was prepared by supplying via line 1 synthesis gas of the following composition to the reactor 2. (all compositions are given in Kmol/h)

Synthesis gas: CO 17.7, H_2 40.9, CO_2 1.8, H_2O 0.6.

At a temperature of 525-575K and a pressure of 40 bar, this synthesis gas, together with recycle of synthesis gas, methanol and CO_2, was converted into dimethyl ether and methanol.

After traversing the process in Figs. 1 and 2, as described hereinabove, 8.1 Kmol/h DME was obtained with a purity of 91%.

CLAIMS

1. A method for the preparation of dimethyl ether from synthesis gas of an HCR value of at least 1.4, comprising
- converting the synthesis gas in a reactor at least partly into a reaction mixture containing dimethyl ether, methanol and water,
- cooling the reaction mixture, thereby forming a first liquid phase containing methanol, dimethyl ether and water, and a first gas phase containing unconverted synthesis gas, CO_2, dimethyl ether, methanol and water,
- washing the first gas phase with a washing liquid substantially containing methanol, thereby forming a second gas phase substantially containing H_2, CO and CO_2, and a second liquid phase substantially containing methanol, dimethyl ether, water and CO_2,
- recovering CO_2 from the first and the second liquid phase and recirculating this CO_2 together with the second gas phase to the reactor, and
- recovering dimethyl ether from the first and the second liquid phase.

2. A method according to claim 1, wherein the first liquid phase is separated in one or more columns into at least a third liquid phase substantially containing methanol and dimethyl ether, and one or more liquid phases and gas phases.

3. A method according to claim 2, wherein at least one liquid phase substantially containing water is formed.

4. A method according to claim 2 or 3, wherein a third gas phase is separated, which contains the greater part of the H_2, CO and CO_2 contained in the first liquid phase.

5. A method according to claims 2-4, wherein from said column a fourth liquid phase, containing methanol, is obtained, which is preferably recirculated to the reactor.

6. A method according to claims 2-5, wherein the second and the third liquid phase, optionally simultaneously, are

separated in a column into a methanol-containing liquid phase, and a dimethyl ether-containing fifth liquid phase.

7. A method according to claim 6, wherein a fourth gas phase is obtained, which contains CO_2 and is recirculated to the reactor.

8. A method according to claim 7, wherein the fifth liquid phase is separated in a column into a CO_2-containing gas phase and a dimethyl ether-containing liquid product stream.

9. A method according to claim 7 or 8, wherein said methanol-containing liquid phase is used as washing liquid for the first gas phase.

10. A method according to claims 1-9, wherein the HCR-value in the synthesis gas is at least 2.0.

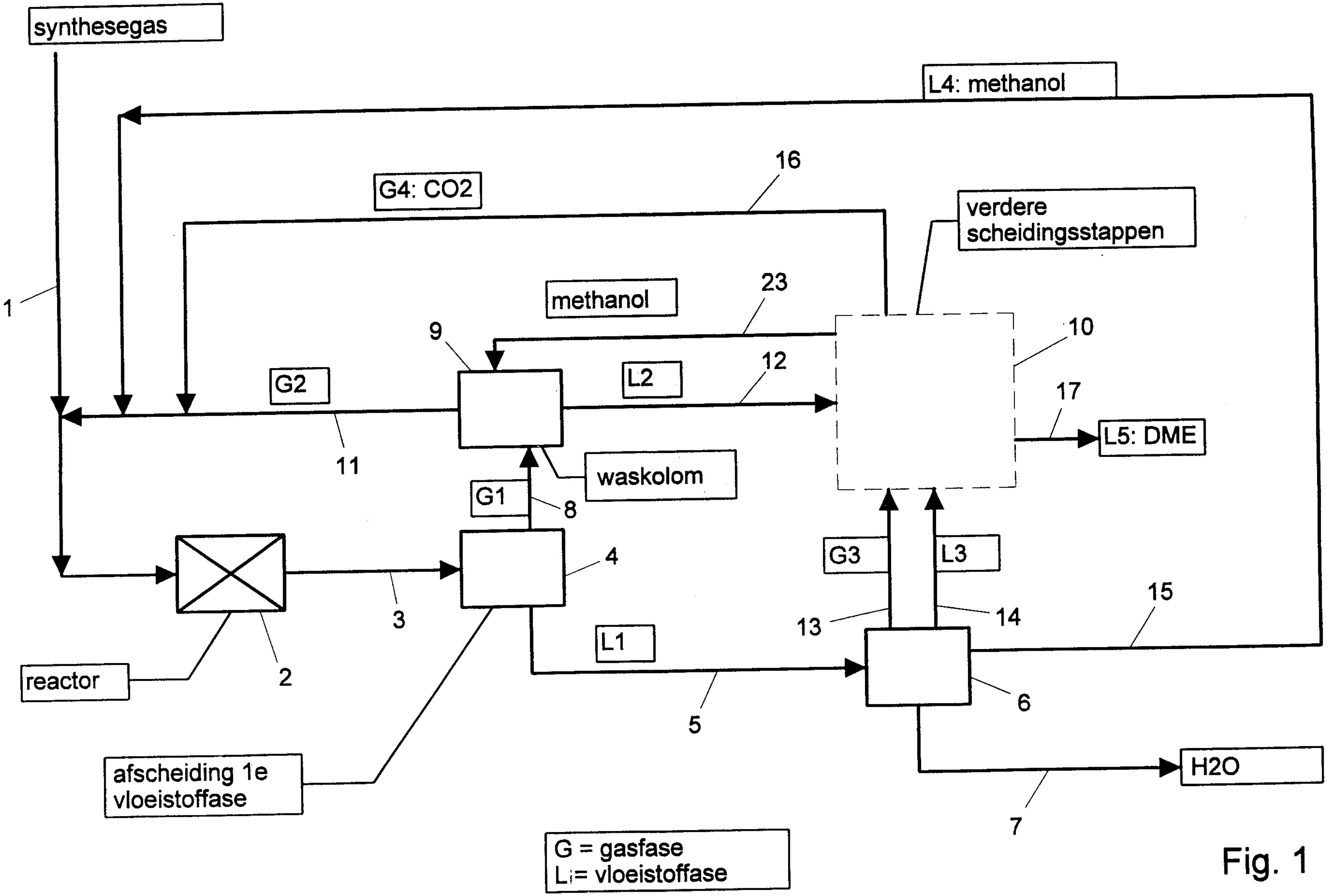
synthesegas
1
L4: methanol
G4: CO2
16
verdere
scheidingsstappen
methanol
23
9
10
G2
L2
12
17
L5: DME
11
waskolom
G1
8
4
G3
L3
3
15
13
14
reactor
2
L1
5
6
afscheiding 1e
vloeistoffase
H2O
7
G = gasfase
L = vloeistoffase

Fig. 1

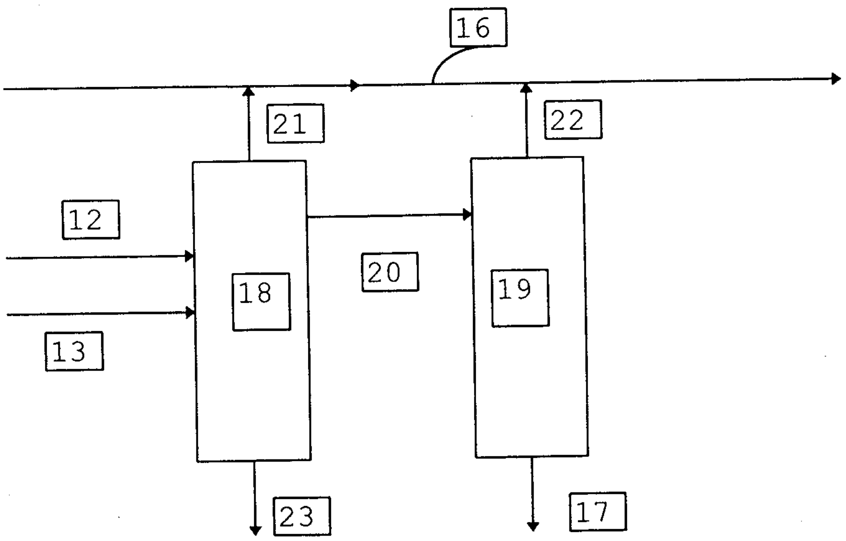

Fig 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 98/00628

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C41/01 C07C43/04

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 C07C

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.
A	DE 42 22 655 A (LEUNA-WERKE) 13 January 1994 cited in the application see the whole document	1-10
A	WO 96 23755 A (HALDOR TOPSOE) 8 August 1996 cited in the application see claims; example	1-10
A	GB 2 253 623 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ) 16 September 1992 see the whole document	1-10

☐ 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 4 February 1999	Date of mailing of the international search report 12/02/1999
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Interr nal Application No
PCT/NL 98/00628

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