There is proposed a process for the production of methanol from a feed stream rich in carbon dioxide, in which a feed stream rich in carbon dioxide is supplied to a methanation stage and is converted there with hydrogen to a stream rich in methane. Along with a feed stream rich in hydrocarbons, the same subsequently is converted to synthesis gas in a reforming stage, which synthesis gas subsequently is converted to the end product methanol. Advantageously, an existing prereforming stage is used as methanation stage.
Process for the Production of Methanol from Carbon Dioxide

Field of the Invention
This invention relates to a multistage process for the production of methanol by conversion of a first feed stream rich in carbon dioxide beside a second feed stream rich in hydrocarbons, for example natural gas or naphtha. This invention furthermore relates to a plant for carrying out the process according to the invention.

Prior art
At present, there is an increasing search for technologies which provide for materially utilizing the greenhouse gas carbon dioxide (CO₂) and convert it to climate-neutral end products. As one of these processes the alternative methanol synthesis is examined, in which - in contrast to classical processes - the used synthesis gas contains no or only small amounts of carbon monoxide (CO) beside hydrogen (H₂), but chiefly or exclusively contains carbon dioxide. Fundamentals of the classical CO-based methanol synthesis can be found for example in Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition, 1998 Electronic Release, chapter "Methanol", sub-chapter 5.2 "Synthesis".

The methanol synthesis from CO₂ and H₂ or synthesis gas rich in CO₂ is possible in principle and has been examined already in earlier papers, for example in the article by H. Gonna and P. Konig, "Producing methanol from CO₂", Chemtech 24 (1994), pp. 36 - 39, wherein in this paper "synthesis gas rich in CO₂" is understood to be synthesis gases with CO₂ concentrations of more than 8 vol-%. As compared to the classical methanol synthesis with synthesis gas rich in CO, however, this process has the disadvantage that the CO₂-based methanol synthesis proceeds at a slower rate. In the 1990s, Lurgi therefore has developed a process which provides an additional adiabatic reactor disposed upstream of the synthesis cycle (see the above-mentioned reference). Furthermore, in the CO₂-based methanol synthesis distinctly more steam is formed, so that there is a higher potential for condensation. A condensation of water on the methanol synthesis catalyst can effect a chemical modification and a mechanical destruction of
the catalyst. Hence it can be seen that the methanol synthesis purely based on carbon dioxide is technically more complex and therefore can be realized only with difficulty in already existing methanol plants.

5 Description of the Invention

The object of the present invention therefore consists in providing a process for the production of methanol by conversion of carbon dioxide, which overcomes the difficulties described above and can easily be integrated into an existing plant for the methanol synthesis by the classical process.

10 The above-mentioned object is solved with the invention according to claim 1 by a process for the production of methanol from a stream rich in carbon dioxide as first feed stream and a stream rich in hydrocarbons as second feed stream, which comprises the following process steps:

15 (a) supplying the first feed stream rich in carbon dioxide to at least one methanation stage and converting the first feed stream with hydrogen under methanation conditions to a stream rich in methane,
(b) supplying the stream rich in methane to at least one synthesis gas production stage and converting the same together with the second feed stream rich in hydrocarbons to a synthesis gas stream containing carbon oxides and hydrogen under synthesis gas production conditions,
(c) supplying the synthesis gas stream to a methanol synthesis stage embedded in a synthesis cycle and converting the same to a product stream comprising methanol under methanol synthesis conditions,
(d) separating the methanol from the product stream comprising methanol and optionally purifying the methanol to a methanol end product stream,
(e) separating a purge stream containing carbon oxides and hydrogen from the methanol synthesis stage.

30 The invention also relates to a plant for carrying out the process according to the invention, which comprises at least one methanation reactor, at least one reforming reactor
equipped with a heating device, at least one methanol synthesis reactor, at least one return conduit for recirculating non-converted synthesis gas to the methanol synthesis reactor, and a methanol separator.

Further advantageous aspects of the process according to the invention can be found in sub-claims 2 to 9, further advantageous aspects of the plant according to the invention in claims 11 to 14.

The invention is based on the finding that the feed stream which is novel as compared to the classical methanol synthesis, i.e. the stream rich in carbon dioxide, is not charged to the methanol synthesis, as taught in the prior art, but is introduced into the process already in the synthesis gas production. Additional hydrogen possibly also is charged there. By means of an additional, constructively simple adiabatic shaft reactor, the CO₂ imported into the process initially is converted to methane by using hydrogen (methanation). After a possible treatment, the hydrogen required for this purpose can originate from the process step according to claim 1 (e) or be obtained from an external source. Alternatively, the additional supply of hydrogen also can be omitted when the process chain includes a prereformation step (prereforming). Since hydrogen is obtained during prereforming, the stream rich in carbon dioxide can be charged to the prereformer and can there be converted to methane. It is advantageous here that the catalysts used for prereforming often also have a sufficient activity for the methanation of carbon dioxide. The methane formed of the two feed streams subsequently is converted to synthesis gas in a manner known per se, wherein reforming processes known from the prior art, such as steam reforming or autothermal reforming (ATR), but also other processes for the production of synthesis gas can be used, such as for example the gasification of petroleum fractions, coal or biomass. At first sight it appears to be absurd to first form methane in the methanation stage and thereupon again convert the same to synthesis gas. Surprisingly, it was found however that the process according to the invention has advantages as compared to the processes described in the prior art, since the reaction can be realized much more easily in terms of process technology. The heat obtained can directly be used in the gas production and need not be coupled
out with great expenditure via heat exchangers. The product water obtained during the 
\( \text{CO}_2 \) methanation according to the reaction equation

\[
\text{CO}_2 + 2 \text{H}_2 = \text{CH}_4 + 2 \text{H}_2\text{O}
\]

has an advantageous effect in the synthesis gas production, as it suppresses the for-

\[\text{mation of soot or the coking of the catalysts used there and in addition can be separated}
\]

in the already existing separator provided downstream of the reformation. In addition, it

thus is no ballast for the methanol synthesis, so that the apparatuses and conduits used

there can be reduced in size with the same performance.

A stream rich in carbon dioxide in the sense of the process according to the invention

can be any gas stream with an increased carbon dioxide concentration, but also a pure

\( \text{CO}_2 \) stream. Therefore, waste gas streams rich in \( \text{CO}_2 \) or enriched in \( \text{CO}_2 \) can be used,

which possibly must be subjected to a pretreatment for removing catalyst poisons, for

example sulfur components. Preferably, the \( \text{CO}_2 \) content of such streams rich in carbon

dioxide is more than 50 vol-%, particularly preferably more than 90 vol-%. Most prefera-

bly, streams rich in carbon dioxide with \( \text{CO}_2 \) contents above 95 vol-% are processed, as

they are obtained for example with the regeneration waste gas of a process for the

physisorptive \( \text{CO}_2 \) separation.

As stream rich in hydrocarbons those feedstocks or feed mixtures can be used which

are also used in conventional synthesis gas production processes, i.e. in particular natu-
rnal gas or evaporated naphtha as typical feedstocks for the reformation. Likewise,

streams rich in hydrocarbons, but also petroleum fractions, coal or biomass can be

used, which under specific conditions each, but known per se to the skilled person, can

be supplied to the synthesis gas production stage.

The reaction conditions and catalysts suitable for carrying out the methanation of \( \text{CO}_2 \)

according to the above reaction equation are known to the skilled person. They are dis-

cussed for example in the International Patent Application WO 2010/006 386 A2 and in

the references cited there.
As synthesis gas production stage, the synthesis gas production processes known from the prior art can be used, such as for example the steam reformation (steam reforming) or the autothermal reformation (ATR), as well as specific gasification processes for non-evaporable streams rich in hydrocarbons, for example heavy petroleum fractions, coal or biomass. Here as well, suitable process conditions are known to the skilled person from the extensive prior art. The relevant prior art is summarized for example in Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition, 1998 Electronic Release, chapter "Gas Production", sub-chapter 2, " Catalytic Reforming of Natural Gas and Other Hydrocarbons ".

A modern two-stage process for the production of methanol, which preferably can also be used when carrying out the process according to the invention, is known for example from EP 0 790 226 B1. The methanol is produced in a cyclic process in which a mixture of fresh and partly reacted synthesis gas first is supplied to a water-cooled reactor and then to a gas-cooled reactor, in each of which the synthesis gas is converted to methanol on a copper-based catalyst. The methanol produced in the process is separated from the synthesis gas to be recirculated after cooling to below the dew point in a cooler. The remaining synthesis gas then is countercurrently passed through the gas-cooled reactor as coolant and preheated to a temperature of 220 to 280 °C, before it is introduced into the first synthesis reactor. A part of the synthesis gas to be recirculated is removed from the process as purge stream, in order to prevent that inert components are enriched within the synthesis cycle. From the European Patent Specification EP 0 790 226 B1 the skilled person also can take further conditions for carrying out the methanol synthesis.

Preferred Aspects of the Invention
A preferred aspect of the process according to the invention provides that the purge stream is supplied to a gas separation stage and in the same is separated into a recirculation stream rich in hydrogen and into a recirculation stream poor in hydrogen. In this way, the valuable constituents of the synthesis gas separated from the methanol synthesis cycle, in particular the hydrogen, can further be utilized.
it is particularly preferred when the recirculation stream rich in hydrogen is recirculated to the at least one methanation stage and/or to the methanol synthesis stage. In this way, the valuable hydrogen can be used for the methanation of the introduced carbon dioxide or for the methanol synthesis.

It is furthermore advantageous when the recirculation stream poor in hydrogen is recirculated to the at least one synthesis gas production stage and is utilized there as fuel. Since the same still has a significant calorific value, it can advantageously be used for the undergrate firing of the reformer furnace of a reforming plant, for example of a steam reforming plant.

An advantageous embodiment of the process according to the invention furthermore provides that the at least one synthesis gas production stage comprises a prereforming stage (prereformer) and a main reforming stage, wherein the first feed stream rich in carbon dioxide is supplied to the prereforming stage and in the same is at least partly converted to methane. A prereformer generally always is used when the feed stream rich in hydrocarbons, which is to be converted to synthesis gas, is natural gas with a significant content of ethane or even higher hydrocarbons. In the prereformer, the higher hydrocarbons are partly or even completely converted to methane. Surprisingly, it is possible without disturbance of the prereforming of the feed stream rich in hydrocarbons to charge the feed stream rich in carbon dioxide and possibly hydrogen to the prereformer, wherein parallel to the prereforming reaction the methanation reaction of the carbon dioxide occurs, so that the same also is converted to methane. An addition of hydrogen often can be omitted, since hydrogen already is formed during the prereformation of the feed stream rich in hydrocarbons. Furthermore energetic advantages are obtained, since the heat requirement of the prereformer for the endothermal prereforming reaction is reduced considerably by the coupling with the exothermal CO\textsubscript{2} methanation.

If additional hydrogen, however, is required, it is provided in a further preferred aspect that the hydrogen additionally charged to the prereforming stage at least partly origi-
nates from the gas separation stage. In this way, the operating material costs are reduced, since less or no expensive hydrogen must be imported into the process.

It is furthermore advantageous when the prereforming stage contains a catalyst which is active both for prereforming and for methanation. This provides logistic advantages in the procurement and handling of the required catalyst. It is particularly favorable that some of the nickel-containing catalysts active for the prereformation of higher hydrocarbons also show a sufficient activity for the methanation of carbon dioxide.

A particular aspect of the plant according to the invention provides that a hydrogen separation plant in the form of a pressure swing adsorption plant or a membrane separation plant is present for the separation of hydrogen from the purge stream. Both processes are known per se. In particular the pressure swing adsorption frequently is used in the product processing downstream of a steam reformation.

It is particularly preferred when the plant according to the invention includes a return conduit for a recirculation stream rich in hydrogen from the hydrogen separation plant to the methanation reactor and/or to the at least one methanol synthesis reactor. In this way, the valuable hydrogen can be used for the methanation of the introduced carbon dioxide or for the methanol synthesis.

A further advantageous aspect of the plant according to the invention is characterized by a return conduit for a recirculation stream poor in hydrogen from the hydrogen separation plant to the heating device of the reforming reactor. Since the recirculation stream poor in hydrogen still has a significant calorific value, it can advantageously be used for the undergate firing of the reformer furnace of a steam reforming plant.

Particular advantages are obtained when the plant according to the invention comprises a prereforming reactor (prereformer) and a main reforming reactor, wherein the prereforming reactor also is utilized as methanation reactor. A prereformer generally always is used when the feed stream rich in hydrocarbons, which is to be converted to synthesis gas, is natural gas with a significant content of ethane or even higher hydro-
carbons. In the prereformer, the higher hydrocarbons are partly or even completely converted to methane. Surprisingly, it is possible without disturbance of the prereforming of the feed stream rich in hydrocarbons to charge the feed stream rich in carbon dioxide and possibly hydrogen to the prereformer, wherein parallel to the prereforming reaction the methanation reaction of the carbon dioxide occurs, so that the same also is converted to methane. An addition of hydrogen often can be omitted, since hydrogen already is formed during the prereformation of the feed stream rich in hydrocarbons. Furthermore energetic advantages are obtained, since the heat requirement of the prereformer for the endothermal prereforming reaction is reduced considerably by the coupling with the exothermal CO₂ methanation.

Exemplary Embodiments

Further developments, advantages and possible applications of the invention can also be taken from the following description of exemplary embodiments and the drawings. All features described and/or illustrated form the invention per se or in any combination, independent of their inclusion in the claims or their back-reference.

In the drawings:

Fig. 1 shows a process for the methanol synthesis according to the prior art as first comparative example,

Fig. 2 shows a process for the methanol synthesis according to the prior art as second comparative example,

Fig. 3 shows the process of the invention according to a first embodiment,

Fig. 4 shows the process of the invention according to a second embodiment.

In the block flow diagram of a process for the methanol synthesis according to the prior art, which is shown in Fig. 1, the feedstock or the feedstock mixture, for example natural gas or naphtha, enters into the process via conduit 10 and is passed to the synthesis gas production stage 11. The same usually is designed as steam reformer or also as autothermal reformer; what is also possible are combinations of the aforementioned types of reformer or also completely different synthesis gas production processes, such as for example the non-catalytic partial oxidation, the gasification of heavy petroleum
fractions or refinery residues, the gasification of coal, the gasification of biomass, each alone or in combination with the aforementioned types of reformer and/or synthesis gas production processes. Suitable operating conditions for these process stages are known to the skilled person.

The feedstock mixture converted to raw synthesis gas leaves the synthesis gas production stage via conduit 12 and - possibly after further conditioning not shown in Fig. 1 - is supplied to the methanol synthesis stage 13. In principle, all of the known processes for the methanol synthesis are usable here, wherein both single-stage and multistage processes can be used; the type of process will therefore not be explained in more detail in Fig. 1. The suitable conditions for operation of the methanol synthesis also are known to the skilled person. The end product methanol is discharged from the process via conduit 14. Furthermore, a purge gas stream is discharged from the methanol synthesis stage via conduit 15, which contains both components inert in the sense of the methanol synthesis, such as methane, nitrogen or noble gases, but also synthesis gas constituents not converted yet, such as carbon oxides or hydrogen. The purge gas stream is supplied to a gas separation stage 16, which can be designed according to processes known per se, for example according to the pressure swing adsorption process (PSA) or according to a membrane separation process. In the gas separation stage a stream enriched in hydrogen is obtained, which is recirculated to the methanol synthesis stage via conduits 17 and 12. Via conduit 18, a gas stream depleted of hydrogen is recirculated to the synthesis gas production stage 11 as fuel gas.

In Fig. 2, a modified process for the methanol synthesis is schematically indicated as block flow diagram, which process is optimized for the processing of synthesis gas rich in CO₂. As described above, such processes have been described already in the prior art. Here, reference is made in particular to the paper by Gonna and Konig, from which the skilled person can take suitable conditions for operating such modified process for the methanol synthesis. Via conduit 12, a feedstock stream containing carbon dioxide and hydrogen enters into the modified methanol synthesis stage 13A, which as compared to methanol synthesis processes from the prior art is optimized with regard to the processing of synthesis gas rich in CO₂. Via conduit 14, the end product methanol is
discharged from the process. Further details of the process, such as for example the synthesis gas production or the processing of the purge gas discharged from the methanol synthesis, are not shown in Fig. 2.

Fig. 3 shows a process for the methanol synthesis according to a first embodiment of the invention as block flow diagram. Again, natural gas or naphtha enters into the process as feedstock mixture via conduit 10 and is passed to the synthesis gas production stage 11, which is designed as reforming stage. In the reforming stage, the steam reformation or the autothermal reformation or a combination of both processes can be used. Again, combinations of the aforementioned types of reformer or also completely different synthesis gas production processes also are possible, such as for example the non-catalytic partial oxidation, the gasification of heavy petroleum fractions or refinery residues, the gasification of coal, the gasification of biomass, each alone or in combination with the aforementioned types of reformer and/or synthesis gas production processes. Suitable operating conditions for said process stages are known to the skilled person.

Via conduit 19, a gas stream rich in CO₂ is supplied to a methanation stage 20, to which hydrogen optionally can be added. The addition of hydrogen is optional, since hydrogen inherent to the process, which is obtained by means of the gas separation stage 16 from the purge gas stream discharged from the methanol synthesis 13 via conduit 15, also is recirculated to the methanation stage 20 via conduit 17A. The addition of hydrogen to the gas stream rich in CO₂ therefore only is required when the hydrogen recirculated via conduit 17A cannot satisfy the stoichiometric demand during the methanation or a recirculation is not possible, because no hydrogen inherent to the process is available yet, for example during start-up of the process. With respect to the selection of suitable process conditions during the methanation, the skilled person can resort to the publications and make required adaptations on the basis of his expert skills. Suitable process conditions are discussed for example in the International Patent Application WO 2010/006386 A2 and in the references cited there.
In the methanation stage 20, the gas stream rich in $\text{CO}_2$ is converted into a product stream rich in methane, which via conduit 21 is supplied to the synthesis gas production stage or reforming stage and in the same converted to raw synthesis gas together with the natural gas or naphtha supplied via conduit 10.

The feedstock mixture converted to raw synthesis gas leaves the synthesis gas production stage or reforming stage via conduit 12 and - possibly after further conditioning not shown in Fig. 3 - is supplied to the methanol synthesis stage 13. In the present exemplary embodiment, a two-stage process for the methanol synthesis with water- and gas-cooled synthesis reactors is particularly preferred, as it is described in the document EP 0 790 226 B1. In principle, however, the methanol synthesis according to a one-stage process also is applicable in the process according to the invention. Details of this process are not shown in Fig. 3. However, since this is a process for processing conventional synthesis gases not rich in $\text{CO}_2$, all single-stage or multistage processes known from the prior art in turn are usable for the methanol synthesis.

The end product methanol is discharged from the process via conduit 14. Furthermore, a purge gas stream is discharged from the methanol synthesis stage via conduit 15, which contains both components inert in the sense of the methanol synthesis, such as methane, nitrogen or noble gases, but also synthesis gas constituents not converted yet, such as carbon oxides or hydrogen. The purge gas stream is supplied to gas separation stage 16, which is designed as pressure swing adsorption process (PSA). What is also possible, however, is the use of other separation processes, for example membrane separation processes. In the gas separation stage a gas stream enriched in hydrogen is obtained, which is recirculated to the methanol synthesis stage via conduits 17 and 12. Furthermore, a partial stream of the gas stream enriched in hydrogen is recirculated to the methanation stage 20 via conduit 17A.

As in the process shown in Fig. 1, a gas stream depleted of hydrogen is recirculated to the synthesis gas production stage 11 as fuel gas via conduit 18.
Fig. 4 shows a further process for the methanol synthesis according to a second embodiment of the invention as block flow diagram. The same largely is analogous to the aspect shown in Fig. 3. Therefore, the features disclosed in connection with the description of Fig. 3 also apply for the process according to the invention as shown in Fig. 4. In the embodiment shown in Fig. 4, however, the feedstock mixture comprising natural gas or naphtha first is supplied to a modified methanation stage 20A, which at the same time operates as prereformer and thus effects a breakdown of higher hydrocarbons to methane. It is advantageous here that the catalysts used for prereforming, for example nickel-based catalysts, often also have a sufficient activity for the methanation of carbon dioxide. Therefore, particular advantages are obtained, as two process steps can be carried out in a single, constructively simple reactor. Possibly, the catalyst volume is to be adapted correspondingly with regard to the targeted conversions of the higher hydrocarbons and the carbon dioxide to methane.

Industrial Applicability

With the invention a process is proposed for the production of methanol from feed streams rich in carbon dioxide, in which the same, together with the classical feedstocks for the methanol synthesis, are converted to the end product methanol. In so far, the process according to the invention represents a contribution to the material utilization of the greenhouse gas carbon dioxide, wherein at the same time feedstocks obtained from fossil raw materials, such as natural gas or naphtha, are saved in part.
List of Reference Numerals

5 [10] conduit
   [12] conduit
   [13] methanol synthesis stage
       [13A] modified methanol synthesis stage
10 [14] conduit
   [15] conduit
   [16] gas separation stage
   [17] conduit
       [17A] conduit
15 [18] conduit
   [19] conduit
   [20] methanation stage
       [20A] modified methanation stage, prereformer
Claims

1. A process for the production of methanol from a stream rich in carbon dioxide as first feed stream and a stream rich in hydrocarbons as second feed stream, comprising the following process steps:
   (a) supplying the first feed stream rich in carbon dioxide to at least one methanation stage and converting the first feed stream with hydrogen under methanation conditions to a stream rich in methane,
   (b) supplying the stream rich in methane to at least one synthesis gas production stage and converting the same along with the second feed stream rich in hydrocarbons to a synthesis gas stream containing carbon oxides and hydrogen under synthesis gas production conditions,
   (c) supplying the synthesis gas stream to a methanol synthesis stage embedded in a synthesis cycle and converting the same to a product stream comprising methanol under methanol synthesis conditions,
   (d) separating the methanol from the product stream comprising methanol and optionally purifying the methanol to a methanol end product stream,
   (e) separating a purge stream containing carbon oxides and hydrogen from the methanol synthesis unit.

2. The process according to claim 1, characterized in that the purge stream is supplied to a gas separation stage and in the same is separated into a recirculation stream rich in hydrogen and into a recirculation stream poor in hydrogen.

3. The process according to claim 2, characterized in that the recirculation stream rich in hydrogen is recirculated to the at least one methanation stage and/or to the methanol synthesis stage.
4. The process according to claim 2, characterized in that the recirculation stream poor in hydrogen is recirculated to the at least one synthesis gas production stage and is utilized there as fuel.

5. The process according to claims 2 to 4, characterized in that the at least one synthesis gas production stage comprises a prereforming stage (prereformer) and a main reforming stage, wherein the first feed stream rich in carbon dioxide is supplied to the prereforming stage and in the same is at least partly converted to methane.

6. The process according to claim 5, characterized in that additional hydrogen is charged to the prereforming stage.

7. The process according to claim 6, characterized in that the hydrogen additionally charged to the prereforming stage at least partly originates from the gas separation stage.

8. The process according to claims 5 to 7, characterized in that the prereforming stage contains a catalyst which is active both for prereforming and for methanation.

9. The process according to claim 8, characterized in that the catalyst of the prereforming stage contains nickel.

10. A plant for carrying out a process according to any of claims 1 to 9, comprising at least one methanation reactor, at least one reforming reactor, equipped with a heating device, at least one methanol synthesis reactor, at least one return conduit for recirculation of non-converted synthesis gas to the methanol synthesis reactor, and a methanol separator.

11. The plant according to claim 10, characterized by a hydrogen separation plant in the form of a pressure swing adsorption plant or a membrane separation plant for the separation of hydrogen from the purge stream.
12. The plant according to claim 11, characterized by a return conduit for a recirculation stream rich in hydrogen from the hydrogen separation plant to the methanation reactor and/or to the at least one methanol synthesis reactor.

13. The plant according to claim 11, characterized by a return conduit for a recirculation stream poor in hydrogen from the hydrogen separation plant to the heating device of the reforming reactor.

14. The plant according to claims 10 to 12, characterized by a prereforming reactor and a main reforming reactor, wherein the prereforming reactor also is utilized as methanation reactor.
Fig. 1

Natural Gas
Naphtha etc.

11 → 12 → 13 → 14 → Methanol

17 → 15 → H₂

16

18

Fig. 2

CO₂ + H₂ → 12 → 13 A → 14 → Methanol
**INTERNATIONAL SEARCH REPORT**

**International application No**

PCT/EP2013/077447

**A. CLASSIFICATION OF SUBJECT MATTER**

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<th>CQ7C31/G4</th>
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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)

C07C C01B

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, ChemAbs Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<td>WO 2010/006386 A2 (UNIV LOUVAIN [BE]; RUIZ PATRICIO [BE]; JACQUEMIN MARC [BE]; BLANGENHOIS) 21 January 2010 (2010-01-21) cited in the application claim 1</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

**Date of the actual completion of the international search**

5 March 2014

**Date of mailing of the international search report**

12/03/2014

**Name and mailing address of the ISA/ European Patent Office, P.O. 5819 Patentison 2 NL-2280 HV Rijswijk**

Tel (31-70) 340-2040, 340-3016

**Authorized officer**

van Bergen, Marc
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