A METHOD AND AN APPARATUS FOR SEPARATING FURFURAL

**Abstract:** In a method and an apparatus furfural is separated from a material stream (3) which is formed in a treatment of a pretreated wood based material (1). The material stream (3) which comprises at least furfural is introduced to a separation column (5). A top vapor condensate (6) is introduced from a top end of the separation column (5) to a decanter (10) in which two liquid phases (9, 11) are separated from each other. An organic phase (9) which comprises at least furfural is recovered, and an aqueous phase (11) is supplied as a reflux to the separation column (5). Further, the invention relates to a furfural based product and chemical product and a use of the organic phase.
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A METHOD AND AN APPARATUS FOR SEPARATING FURFURAL

FIELD

The invention relates to a method and an apparatus for separating furfural. Further, the invention relates to a furfural based product and a chemical product. Further, the invention relates to a use of organic phase.

BACKGROUND

It is known different methods for forming carbohydrates and lignin from different raw materials, such as biomass. Many bio-refinery processes, e.g. a hydrolysis, generate lignin and sugars after the treatment of the biomass. It is known that sugars streams comprise also other chemical compounds, e.g. furfural.

OBJECTIVE

The objective of the invention is to disclose a method for separating furfural. Another objective is to remove furfural from products formed in a treatment of wood based material. Another objective is to recover furfural from the wood based material. Another objective is to recover other chemical compound, such as carboxylic acid, from the wood based material.

SUMMARY

The method for separating furfural is characterized by what is presented in claim 1.

The apparatus for separating furfural is characterized by what is presented in claim 15.

The furfural based product is characterized by what is presented in claim 22.
The chemical product is characterized by what is presented in claim 23.

The use of the organic phase is characterized by what is presented in claim 24.

**BRIEF DESCRIPTION OF THE DRAWINGS**

The accompanying drawings, which are included to provide a further understanding of the invention and constitutes a part of this specification, illustrate some embodiments of the invention and together with the description help to explain the principles of the invention. In the drawings:

Fig. 1 is a flow chart illustration of a method according to one embodiment.

**DETAILED DESCRIPTION**

In a method for separating furfural from a material stream (3), which is formed in a treatment of a pretreated wood based material (1), the material stream (3) which comprises at least furfural is introduced to a separation column (5), a top vapor condensate (6) is introduced from a top end of the separation column (5) to a decanter (10) in which two liquid phases (9, 11) are separated from each other, an organic phase (9) which comprises at least furfural is recovered, and an aqueous phase (11) is supplied as a reflux to the separation column (5).

One embodiment of the method is shown in Fig 1.

The apparatus for separating furfural comprises at least one feeding device for introducing a material stream (3) which comprises at least furfural to a separation column (5), at least one separation column (5) in which at least a top vapor condensate (6) is formed, at least one decanter (10) to which the top
vapor condensate (6) is introduced from a top end of the separation column (5) and in which two liquid phases (9,11) are separated from each other and from which an organic phase (9) which comprises at least furfural is supplied out and recovered, and at least one recirculating device for supplying an aqueous phase (11) from the decanter as a reflux to the separation column (5).

In this context, a material stream (3) means any material stream which is formed, e.g. by separating, collecting or recovering, from a pretreated wood based material (1) and which comprises at least furfural. The material stream (3) may comprise also organic acids, such as acetic acid or other organic acids. In one embodiment, the material stream comprises at least water, furfural and organic acids. The material stream may comprise also other components. In one embodiment, the material stream (3) may be the pretreated wood based material or, preferably, a fraction of the pretreated wood based material. In one embodiment, the material stream (3) may be formed from the pretreated wood based material after any suitable treatment stage of the pretreated wood based material. The material stream (3) may be in the form of steam, such as vapor, or liquid, such as condensate.

In one embodiment, the pretreated wood based material (1) comprises at least carbohydrates, such as C5 and/or C6 carbohydrates, and furfural. In one embodiment, the pretreated wood based material (1) comprises at least C5 carbohydrates. In one embodiment, the pretreated wood based material (1) comprises at least C5 and C6 carbohydrates. Further, in one embodiment, the pretreated wood based material comprises organic acids. Further, the pretreated wood based material (1) may comprise also other components, such as side and degradation products. In one embodiment, the pretreated wood
based material (1) is formed from raw material. In one embodiment, the pretreated wood based material (1) is formed in a wood-to-sugar process. In one embodiment, the raw material comprises at least one of wood based material, wood, lignocellulosic biomass, agricultural residues, bagasse based material, sugarcane bagasse, corn based material, corn stover, wheat straw, rice straw, woody biomass, woody perennials, vascular plants, recycled brown board or deinking pulp, or their mixtures or their combinations. Preferably, the raw material is cellulose based material. The raw material may comprise lignin, lignocellulose, cellulose, hemicellulose, glucose, xylose and/or extractives. Further, the raw material may comprise other inherent structural components of biomass as well as foreign components such as enzymes or chemicals. In one embodiment, the raw material comprises wood based material or a mixture comprising wood based material. In one embodiment, the raw material is wood based material or a mixture comprising wood based material. In one embodiment, the wood based material is selected from hardwood, softwood or their combination. In one embodiment, the raw material comprises plant pieces, e.g. wood pieces. In one embodiment, the raw material comprises lignin, cellulose, carbohydrates and some chemical compounds. In one embodiment, the raw material may be treated by means of any suitable method for forming the pretreated wood based material (1). In one embodiment, the pretreated wood based material (1) is formed from the raw material which preferably is treated to dissolve at least a part of hemicellulose or a main part of hemicellulose. In one embodiment, the raw material is pre-treated, preferably by means of a suitable pretreatment stage which may be selected from the group comprising physical pretreatment, such as milling, extrusion, microwave pretreatment, ultra-
sound pretreatment and freeze pretreatment, chemical pretreatment, such as acid pretreatment, alkaline pretreatment, ionic liquid pretreatment, organosolv pretreatment and ozonolysis, physico-chemical pretreatment, such as steam explosion pretreatment, ammonia fiber explosion pretreatment, \( \text{CO}_2 \) explosion pretreatment, liquid hot water pretreatment and wet oxidation, biological pretreatment and their combinations. In one embodiment, the raw material is treated by the hydrolysis, e.g. acid hydrolysis, autohydrolysis, thermal hydrolysis, supercritical hydrolysis and/or subcritical hydrolysis, in which at least a part of hemicellulose is separated from the raw material in connection with the hydrolysis. In one embodiment, the raw material is treated by the steam explosion, in which hemicelluloses are treated and in which at least a part of polysaccharides of the hemicelluloses degrade into monosaccharides and oligosaccharides by means of a hydrolysis and in which pressure is rapidly released. In one embodiment, the raw material is treated by the hydrolysis and by the steam explosion in one or more steps. In one embodiment, the raw material is treated by the catalytic pretreatment, e.g. by using acid or base as catalyst. In the pretreatment stage the raw material enters the reactor unit where the pretreatment takes place. The raw material can be treated by means of one or more pretreatment. The treated raw material can be then supplied directly, via an intermediate step, via an additional treatment step or via an intermediate storage as a pretreated wood based material (1) to a desired treatment stage and/or to a furfural separation. Further, in one embodiment, the raw material can be dewatered, e.g. by dewatering presses, and/or washed in one or two or more stages. The dewatering makes possible to separate sugar based streams.
In one embodiment, the pretreated wood based material (1) is supplied to a concentration stage (2) for forming a concentrated carbohydrate based material (4) and the material stream (3). The pretreated wood based material (1) may be treated in one or more than one concentration stage (2). The material stream may be in the form of steam or liquid after the concentration stage (2). In one embodiment, the material stream (3) is a vapor or a condensate of vapor from the concentration stage (2). In one embodiment, the material stream (3) is a top vapor of the concentration stage (2). Preferably, furfural accumulates into the material stream (3) during the concentration stage (2). In one embodiment, apparatus comprises at least one concentration stage (2) which comprises at least one concentration device and in which the pretreated wood based material is concentrated in order to form the concentrated carbohydrate based material (4) and the material stream (3). In one embodiment, apparatus comprises more than one concentration stage (2) which comprises at least one concentration device. In one embodiment, apparatus comprises more than one concentration devices. In one embodiment, the concentration stage (2) is an evaporation stage, e.g. a vacuum evaporation, multi-effect evaporation, forced circulation evaporation, film evaporation, or other suitable evaporation or their combinations. In one embodiment, the concentration stage (2) comprises at least one evaporation device. In one embodiment, the evaporation device is selected from the group comprising a vacuum evaporation device, mechanical vapor compressor, thermal vapor compressor, multi-effect evaporation device, forced circulation evaporation device, film evaporator, plate type evaporator, tube evaporator, batch evaporator, continuous evaporator and their combinations.
In this context, the concentrated carbohydrate based material (4) comprises at least C5 carbohydrates. In one embodiment, the concentrated carbohydrate based material (4) comprises C5 and C6 carbohydrates. The concentrated carbohydrate based material (4) may comprise also other agents or components. In one embodiment, the concentrated carbohydrate based material (4) is further concentrated by means of the top vapor condensate (6) after the separation column (5) in a post-evaporation stage.

The material stream (3) is introduced to the separation column (5). In one embodiment, the material stream (3) is fed to the separation column (5) at temperature of 70 - 80 °C. The material stream (3) may be introduced to any suitable part of the separation column. In one embodiment, the material stream (5) is introduced to the top part of the separation column (5). In one embodiment, the material stream (5) is introduced to the bottom part of the separation column (5). In one embodiment, the material stream (5) is introduced to the middle part of the separation column (5). In one embodiment, the separation column (5) comprises trays or plates. In one embodiment, the separation column (5) comprises 5 - 20 stages or trays. In one embodiment, the separation column (5) comprises one or more than one columns.

In one embodiment, the separation column (5) is based on a hetero-azeotropic distillation. In one embodiment, an azeotropic mixture comprises at least furfural and water. In one embodiment, the separation column (5) is a hetero-azeotropic distillation device. In the hetero-azeotropic distillation two liquid phases are on the plate. The top vapor condensate (6) splits in two liquid phases which can be separated in the decanter (10). In one embodiment, the top vapor condensate (6) comprises at least furfural and water. In one embodi-
ment, the hetero-azeotropic distillation is a batch distillation process. In one embodiment, the hetero-azeotropic distillation is a continuous distillation process.

In one embodiment, the material stream (3) is introduced to the separation column (5) in countercurrent to a vapor formed in the separation column (5). In one embodiment, the vapor strips out furfural from the material stream leading to an increased concentration of furfural at the top end of the separation column (5).

In one embodiment, the temperature in the separation column (5) is 90 - 130 °C, in one embodiment 95 - 105 °C and in one embodiment 115 - 125 °C.

In one embodiment, the pressure in the separation column (5) is 0.5 - 2.5 bar, in one embodiment 0.5 - 1.5 bar and in one embodiment 1.5 - 2.5 bar.

In one embodiment, a by-product (7) is discharged out from the separation column (5). In one embodiment, the by-product (7) is discharged from the bottom end of the separation column (5). The by-product (7) may comprise water, e.g. washing water or dilution water, and/or organic acids, e.g. acetic acid. In one embodiment, the by-product (7) is a water based stream. In one embodiment, the by-product (7) is a residue from the distillation.

In one embodiment, at least one carboxylic acid fraction is recovered in the separation column (5). In one embodiment, an acetic acid fraction is recovered in the separation column (5). The carboxylic acid fraction may be recovered from the bottom of the separation column (5) or from any suitable part, such as from a desired tray or plate, of the separation column (5).

In one embodiment, the top vapor condensate (6) is cooled in a cooling stage (8) before the decanter
In one embodiment, the apparatus comprises at least one cooling device \( (8) \) in which the top vapor condensate \( (6) \) is cooled before the decanter \( (10) \). The cooling device may be any suitable cooling device, e.g. a heat exchanger or condenser.

Preferably, in the decanter \( (10) \) the top vapor condensate \( (6) \) splits in two liquid phases. In one embodiment, the top vapor condensate \( (6) \) is supplied to a bottom part of the decanter \( (10) \). In one embodiment, temperature is 20 - 30 °C, in one embodiment 23 - 28 °C, during the decantation in the decanter \( (10) \). In one embodiment, pressure is 0.5 - 2.5 bar, in one embodiment 0.5 - 1.5 bar, in one embodiment 1.5 - 2.5 bar, during the decantation in the decanter \( (10) \). In one embodiment, the organic phase \( (9) \) is recovered from an upper part of the decanter and the aqueous phase \( (11) \) is discharged from the bottom part of the decanter. In one embodiment, the separation surface of the organic phase \( (9) \) and the aqueous phase \( (11) \) is adjusted to a suitable level during the decantation in the decanter \( (10) \). Preferably, the organic phase \( (9) \) comprises furfural in high purity, i.e. the organic phase is a furfural rich phase. In one embodiment, by means of the ratio of the organic phase \( (9) \) and the aqueous phase \( (11) \) and by means of the process conditions can be adjusted the purity of the organic phase \( (9) \).

In one embodiment, the apparatus comprises at least one recovery device for recovering the organic phase \( (9) \) which comprises at least furfural. Any suitable device can be used as the recovery device. In one embodiment, the recovery device is selected from the group comprising assembly, outlet, pipe, tube, duct, discharge outlet, discharge valve, discharge channel, conduit, other suitable device, tank, vessel and their combinations.
In one embodiment, the apparatus comprises at least one furfural purification stage comprising at least one purification device after the decanter (10) in which the organic phase (9) is purified and/or concentrated. In one embodiment, the purification device may be an additional distillation device or the second separation column (5), e.g. hetero-azeotropic distillation device, or other suitable device.

In one embodiment, the organic phase (9) comprises furfural over 70 % by weight, preferably over 80 % by weight, more preferably over 90 % by weight and most preferably over 95 % by weight.

The aqueous phase (11) is recirculated to the separation column (5). The aqueous phase (11) may comprise water and organic acids, such as acetic acid. Further, in one embodiment, the aqueous phase (11) may comprise also furfural. Any suitable device can be used as the recirculating device. In one embodiment, the recirculating device is selected from the group comprising assembly, pump, outlet, inlet, pipe, tube, duct, discharge outlet, discharge valve, discharge channel, conduit, other suitable feeding device, other suitable device and their combinations.

In one embodiment, the aqueous phase (11) is supplied as the reflux to the separation column (5) in counter-current to the material stream (3).

In one embodiment, the method is based on a continuous process. In one embodiment, the apparatus is a continuous apparatus. In one embodiment, the method is based on a batch process. In one embodiment, at least a part of the apparatus is a batch apparatus.

A furfural based product may be formed according to any method or apparatus defined above. In one embodiment, the furfural based product is in the form of liquid.
A chemical product comprising a carboxylic acid fraction may be formed according to any method or apparatus defined above. In one embodiment, the chemical product is in the form of liquid. The organic phase (9) may be used as a source material in an additional treatment, chemical treatment, polymerization process, manufacture of a chemical, plastic, cellulose acetate or varnish, or other suitable process, or as a component in a fuel or combustion material, or their combinations.

The method and the apparatus provide furfural and also carbohydrates with good quality. By means of the method and apparatus carbohydrate based streams can be purified and waste water treatment plant loading can be reduced and valuable components can be recovered.

The method and the apparatus provide an industrially applicable, simple and affordable way of separating and recovering furfural and recovering also other chemicals. The method or the apparatus is easy and simple to realize as a production process. The method and the apparatus are suitable for use in connection with the manufacture of the different lignin and carbohydrate products from different raw materials.

EXAMPLES

Some embodiments of the invention are described in more detail by the following examples with reference to accompanying drawing.

Example 1

In this example, furfural is separated from a material stream (3) according to a process of Fig.1.

The material stream (3) has been formed in a treatment of a pretreated wood based material (1) com-
prising at least carbohydrates and furfural. The pre-
treated wood based material has been formed from raw
material by pretreating the raw material. The raw ma-
terial is wood based material or a mixture comprising
wood based material. The material stream (3) is in the
form of steam or liquid.

The apparatus for separating furfural compris-
es at least one feeding device for introducing a mate-
rial stream (3) which comprises at least furfural to a
separation column (5), at least one separation column
(5) in which at least a top vapor condensate (6) is
formed, and at least one decanter (10) to which the
top vapor condensate (6) is introduced from a top end
of the separation column (5) and in which two liquid
phases (9,11) are separated from each other. Further,
the apparatus comprises at least one recovery device
for recovering an organic phase (9) which comprises at
least furfural and at least one recirculating device
for supplying an aqueous phase (11) as a reflux to the
separation column (5).

The separation column (5) is preferably based
on a hetero-azeotropic distillation in which an azeo-
tropic mixture comprises at least furfural and water.

The top vapor condensate (6) comprises at
least furfural and water. Carboxylic acid fraction or
fractions may be recovered in the separation column
(5). Further, a by-product (7) may be discharged out
from the separation column (5). The by-product (7) may
comprise water and/or organic acids, e.g. acetic acid.

Preferably, the material stream is introduced
to the separation column (5) in counter-current to a
vapor formed in the separation column (5). Preferably,
the aqueous phase (11) is supplied as the reflux to
the separation column (5) in counter-current to the
material stream (3).
Further, the apparatus may comprise a cooling device (8) in which the top vapor condensate (6) is cooled before the decanter (10).

Further, the apparatus comprise at least one concentration stage (2) comprising at least one concentration device, e.g. an evaporation device, in which the pretreated wood based material is concentrated in order to form a concentrated carbohydrate based material (4) and the material stream (3). The material stream (3) is collected during the concentration. The material stream may be a vapor or a condensate of vapor from the concentration device.

Further, the apparatus may comprise at least one furfural purification stage comprising at least one purification device after the decanter (10) in which the organic phase (9) is purified or concentrated.

Example 2

In this example, a furfural separation was studied.

The furfural was separated from a material stream (3) according to the process presented in Fig. 1.

A pretreated wood based material (1), 80 t/h, comprising at least C5 carbohydrates, such as xylose 50 g/1, and 0.4 w-% (4 g/1) furfural, was supplied to an evaporation stage (2) which comprises at least one evaporation device. The pretreated wood based material was formed from raw material by pretreating with diluted acid the raw material which is wood based material.

In the evaporation stage (2) the pretreated wood based material was treated and concentrated in order to form about 43.5 t/h concentrated carbohydrate based material (4) and about 36.5 t/h material stream.
(3) which comprises at least furfural. The pressure in the evaporation stage was about 0.5 bar. The material stream (3) was collected during the concentration. The material stream was in the form of a vapor after the evaporation device. The temperature of the material stream after the evaporation device was 81.30 °C.

The material stream (3) which comprises at least furfural was introduced by means of a feeding device to a separation column (5) which is a heteroazeotropic distillation column. A diameter of the distillation column was about 3 meters, and the distillation column comprised 15 stages. Temperature was 99.34 °C in a top part of the distillation column and 99.98 °C in a bottom part of the distillation column. Pressure was about 1.0 bar in the distillation column. In the separation column (5) a top vapor condensate (6) was formed. An azeotropic mixture comprised at least furfural and water. The top vapor condensate (6) comprised at least furfural and water. Carboxylic acid fraction or fractions may be recovered in the separation column (5). Further, a by-product flow (7) which is a water based flow was discharged out from the bottom of the separation column (5).

The top vapor condensate (6) was introduced from a top end of the separation column (5) to a cooling device (8) in which the top vapor condensate (6) was cooled. The temperature of the condensate (6) was 50 °C after the cooling device (8). After the cooling the condensate (6) was introduced to a decanter (10) in which two liquid phases, i.e. an organic phase (9) and an aqueous phase (11), were separated from each other. The organic phase (9) which comprises mainly furfural was recovered. The organic phase contained 92.1 w-% furfural The aqueous phase (11) which comprises mainly water was recirculated as a reflux to the separation column (5).
The material stream was introduced to the separation column (5) in counter-current to a vapor formed in the separation column (5). Further, the aqueous phase (11) was supplied as the reflux to the separation column (5) in counter-current to the material stream (3).

Further, the organic phase (9) may be purified by means of at least one furfural purification device after the decanter (10).

The method and apparatus according to the present invention is suitable in different embodiments to be used in different furfural separation processes and/or chemical recovery processes. Further, the method and apparatus according to the present invention is suitable in different embodiments to be used for producing the most different kinds of carbohydrate fractions and chemical products from different raw materials.

The invention is not limited merely to the example referred to above; instead many variations are possible within the scope of the inventive idea defined by the claims.
CLAIMS

1. A method for separating furfural from a material stream (3) which is formed in a treatment of a pretreated wood based material (1), wherein
   - the material stream (3) which comprises at least furfural is introduced to a separation column (5),
   - a top vapor condensate (6) is introduced from a top end of the separation column (5) to a de-canter (10) in which two liquid phases (9,11) are separated from each other,
   - an organic phase (9) which comprises at least furfural is recovered, and
   - an aqueous phase (11) is supplied as a reflux to the separation column (5).

2. The method according to claim 1, wherein the material stream (3) is in the form of steam or liquid.

3. The method according to claim 1 or 2, wherein the pretreated wood based material (1) comprises at least carbohydrates and furfural.

4. The method according to any one of claims 1 to 3, wherein the pretreated wood based material (1) is supplied to a concentration stage (2) for forming a concentrated carbohydrate based material (4) and the material stream (3).

5. The method according to any one of claims 1 to 4, wherein the concentration stage (2) is an evaporation stage.

6. The method according to any one of claims 1 to 5, wherein the material stream (3) is introduced to the separation column (5) in counter-current to a vapor formed in the separation column (5).
7. The method according to any one of claims 1 to 6, wherein the separation column (5) is based on a hetero-azeotropic distillation.

8. The method according to claim 7, wherein an azeotropic mixture comprises at least furfural and water.

9. The method according to any one of claims 1 to 8, wherein the top vapor condensate (6) comprises at least furfural and water.

10. The method according to any one of claims 1 to 9, wherein at least one carboxylic acid fraction is recovered in the separation column (5).

11. The method according to any one of claims 1 to 10, wherein the top vapor condensate (6) is cooled in a cooling stage (8) before the decanter (10).

12. The method according to any one of claims 1 to 11, wherein the organic phase (9) comprises furfural over 70 % by weight, preferably over 80 % by weight, more preferably over 90 % by weight and most preferably over 95 % by weight.

13. The method according to any one of claims 1 to 12, wherein the aqueous phase (11) is supplied as the reflux to the separation column (5) in counter-current to the material stream (3).

14. The method according to any one of claims 1 to 13, wherein the pretreated wood based material (1) is formed from raw material which is wood based material or a mixture comprising wood based material.

15. An apparatus for separating furfural from a material stream (3) which is formed in a treatment of a pretreated wood based material (1), wherein the apparatus comprises
   - at least one feeding device for introducing the material stream (3) which comprises at least furfural to a separation column (5),
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- at least one separation column (5) in which at least a top vapor condensate (6) is formed,
- at least one decanter (10) to which the top vapor condensate (6) is introduced from a top end of the separation column (5) and in which two liquid phases (9,11) are separated from each other and from which an organic phase (9) which comprises at least furfural is supplied out and recovered, and
- at least one recirculating device for supplying an aqueous phase (11) as a reflux to the separation column (5).

16. The apparatus according to claim 15, wherein the apparatus comprises at least one concentration stage (2) in which the pretreated wood based material is concentrated in order to form a concentrated carbohydrate based material (4) and the material stream (3).

17. The apparatus according to claim 15 or 16, wherein the concentration stage (2) comprises at least one evaporation device.

18. The apparatus according to any one of claims 15 to 17, wherein the separation column (5) is a hetero-azeotropic distillation device.

19. The apparatus according to any one of claims 15 to 18, wherein the apparatus comprises at least one cooling device (8) in which the top vapor condensate (6) is cooled before the decanter (10).

20. The apparatus according to any one of claims 15 to 19, wherein the apparatus comprises at least one recovery device for recovering the organic phase (9) which comprises at least furfural.

21. The apparatus according to any one of claims 15 to 20, wherein the apparatus comprises at least one furfural purification stage after the decanter.
in which the organic phase (9) is purified and/or concentrated.

22. A furfural based product comprising the organic phase (9) which has been formed by the method according to any one of claims 1 to 14.

23. A chemical product comprising a carboxylic acid fraction which has been formed by the method according to any one of claims 1 to 14.

24. A Use of the organic phase (9) obtainable by the method according to any one of claims 1 to 14, wherein the organic phase (9) is used as a source material in an additional treatment, chemical treatment, polymerization process, manufacture of a chemical, plastic, cellulose acetate or varnish, or other suitable process, or as a component in a fuel or combustion material, or their combinations.
# INTERNATIONAL SEARCH REPORT

## A. CLASSIFICATION OF SUBJECT MATTER

**INV. C07D307/50**

Add.

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07D

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Electronic database consulted during the international search (name of database and, where practical, search terms used)

EPO-Internal, BIOSIS, CHEM ABS Data, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>WO 2012/057625 A2 (UNIV DELFT TECH [NL]; DE JONG W; EBREN [NL]; MARCOTULLIO GIANLUCA [NL]) 3 May 2012 (2012-05-03) page 8, paragraph 1; figure 1 (Scheme II)</td>
<td>1-24</td>
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<td>X</td>
<td>WO 2009/130386 AI (KEMI RA OYJ [FI]; REUNANEN JARMO [FI]; 0INAS PEKKA [FI]; NISSINEN TIMO) 29 October 2009 (2009-10-29) page 15, line 18 - page 16, line 12; claim 7; figure 1</td>
<td>1-24</td>
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<td>X</td>
<td>WO 2016/020269 AI (CLARIANT INT LTD [CH]) 11 February 2016 (2016-02-11) example; page 7, paragraphs 5, 6; claims 1-5, 12, 14, 16; figure 2B</td>
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Date of the actual completion of the international search: 16 February 2018

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