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- (54) **Title:** METHOD AND APPARATUS FOR FURFURAL PRODUCTION

(57) **Abstract:** The invention concerns a process for the production of furfural from pentoses and/or water soluble pentosans, comprising the steps of feeding an aqueous pentose solution containing one or more pentoses or soluble pentosans to the bottom of a reaction column to produce an aqueous liquid upflow; heating the bottom part of the column using a heat exchanger to produce a steam upflow in the column; recovering a vapour product stream containing water and furfural from the top of the column; and condensing the vapour product stream, thereby obtaining an aqueous furfural containing product solution as the condensate.



Title: Method and Apparatus for Furfural Production

The invention is directed to a process for the production of furfural
5 (or 2-furancarboxaldehyde) from pentoses and/or water soluble pentosans.

Furfural is a chemical intermediate readily available from
lignocellulosic biomass, and it is industrially produced since 1921 mainly
from residues of agriculture. Furfural offers alternative ways for producing
numerous materials as well as new generation biofuels. Potential and
10 upcoming markets for furan resins cover a wide spectrum with massive
potential utilization, from wood preservatives to construction materials. In
the past furfural has been already used as starting material for the
production of important chemical intermediates like THF. Favourable
balances between oil prices and furfural availability, as well as green
15 oriented policies, are likely to drive a switch back to the furfural based
routes.

As far as the energy sector is concerned, direct hydrogenation
derivatives of furfural also have a high potential as alternative liquid fuels
and fuel extenders. 2-Methyltetrahydrofuran (MTHF) has been proven to
20 show superior characteristics as fuel extender in regular gasoline, as well as
in alternative fuels formulations based on ethanol (P-series fuels). 2-
Methylfuran and tetrahydrofurfuryl alcohol (THFA) could also be potential
candidates as biomass derived octane enhancer, and as diesel fuel additive.
Furthermore, by controlled reactions involving furfural, such as aldol
25 condensation, alkylation and etherification, larger molecules may be
obtained, that can undergo subsequent hydrogenation/hydrogenolysis to
molecules with superior fuel characteristics, such as higher alkanes.

Current furfural production processes are energy intensive and
costly. Moreover, they exhibit relatively low yields, 50-60% of the
30 theoretical, and they are poorly integrated with processes aimed at
valorising the entire biomass feedstock. This makes furfural less suitable for
the fuel industry at the moment, and not always cost competitive with oil

derivatives in the chemical industry. The development of novel production processes is needed in order to unlock the potential of this biomass derived platform chemical.

In WO 81/00407 (US-A 4366322) a process for the production of
5 furfural is described, wherein pentoses are converted into furfural at atmospheric pressure and a temperature below 110°C, in a strong acid medium (6N acid). This process shows a low yield and produces a large amount of byproducts. It also has a large energy requirement.

In DE 740602 the production of furfural has been described, using
10 a recycle of part of the product stream to the bottom of the column. This process shows low yield and substantial by-product formation.

Traditional processes employ a large share of their primary energy input to produce high pressure steam to strip out furfural from the reacting system, and for its subsequent purification by distillation. The total energy
15 consumption in such processes ranges from 15 to 50 ton of steam per ton of furfural produced. Nevertheless, the direct reduction of steam usage is usually detrimental for the furfural yield from biomass, and for this reason, despite the related energy costs, plentiful steam stripping is crucial in furfural production.

20 WO 2012/057625 addresses the above problems by providing a process for the production of furfural from pentoses and/or water soluble pentosans, said process comprising converting the said pentoses and/or water soluble pentosans in aqueous solution in a first step to furfural and in a second step feeding the aqueous solution containing furfural obtained in
25 the first step to the top of a distillation column to produce an aqueous, liquid downflow, which column is heated at the bottom part thereof, using at least one reboiler to produce an upflow steam flow, recovering a water and furfural containing vapour product stream from the top of the said column, compressing the said vapour flow and condensing it on the hot side of the
30 reboiler at the bottom of the said column to produce sufficient steam in the

said bottom part of the column to produce the said upflow steam flow, and to recover an aqueous furfural containing solution as the condensate in the reboiler.

However, an as of yet unrecognized problem of the above process is
5 that a significant product loss was observed such that no optimal yield can be achieved.

Accordingly, it is an object of the invention to reduce or even avoid product loss in the process described in WO 2012/057625, thereby increasing its yield.

10 A further object of the invention is to provide a process for the production of furfural from pentoses requiring less energy, yet allowing for abundant steam stripping.

This object was met by providing a process for the production of furfural from pentoses and/or water soluble pentosans by contacting a liquid
15 flow of pentose solution containing one or more pentoses or soluble pentosans in co-current flow with a steam flow containing water and furfural.

More in particular, the invention is directed to a process for the production of furfural from pentoses and/or water soluble pentosans,
20 wherein the process comprises the steps of

- feeding an aqueous pentose solution containing one or more pentoses or soluble pentosans to the bottom of a reaction column to produce an aqueous liquid upflow; and
- heating the bottom part of the column using a heat exchanger to produce a
25 steam upflow in the column; and
- recovering a vapour product stream containing water and furfural from the top of the column; and
- condensing the vapour product stream, thereby obtaining an aqueous furfural containing product solution as the condensate.

The inventors realized that significant product loss will occur in the process of WO 2012/057625 caused by undesirable reactions involving furfural, sugars and/or other reaction intermediates. The inventors unexpectedly found that reactions that lead to product loss (abbreviated hereinafter as 'loss reactions') can be reduced or even avoided when contacting the liquid flow and the steam flow co-currently. Accordingly, the process of the invention uses an upflow for both the liquid and the vapour stream. During the upflow, pentose and/or pentosans will be converted to furfural and the steam upflow will be enriched in furfural.

Figures 1 and 2 show a schematic representation of two embodiments of the method of the invention.

Figure 3a shows a schematic representation of an embodiment of the column reactor of the invention. Figure 3b shows a cross-section of the column reactor at positions A, B and C.

Figure 4 shows two graphs estimating the furfural and sugar concentrations in a co-current and counter-current process.

The inventors believe that loss reactions will in particular take place in the presence of high concentrations of furfural and high concentrations of pentose/pentosans. The inventors further realized that when using a traditional distillation column set-up, as was done in WO 2012/057625, the above-mentioned concentrations will both be very high in proximity to the top of the distillation column, thereby enhancing the loss of furfural. However, when flowing the liquid stream (liquid flow) and vapour stream (steam flow) co-currently, such conditions can be avoided. As a result, loss reactions will be reduced and the total furfural yield will increase.

Conventional distillation is amongst others based on establishing a reflux flow, wherein the liquid must flow in downward direction through the column. Accordingly, when using such conventional distillation, the aqueous pentose solution is fed to the top of the distillation column and then flowing

down, while the vapour is produced at the bottom of the distillation column and flowing up. The liquid downflow will have the highest concentration of pentose and pentosans at the top of the column and the concentration will decrease towards to the bottom of the column as more pentose and pentosan
5 will be converted to furfural. The steam upflow will also have the highest furfural concentration in proximity to the top of the column, as more furfural, while being produced, is transferred to the vapour upflow. Accordingly, when the liquid downflow is contacted with the steam upflow at the top of the column, both furfural and pentose/pentosan concentrations
10 are high.

By producing an aqueous liquid upflow (*i.e.* an aqueous liquid stream that flows upward) and a steam upflow (*i.e.* a vapour stream containing water and furfural that flows upward), the liquid and steam streams both flow co-currently.

15 In the co-current flow the vapour stream still leaves the column from the top, but the liquid feed enters the column from the bottom. In this way the concentration of pentoses and/or pentosans will decrease from the bottom to the top of the column, opposite to the furfural concentration. The area of the column where losses may take place is thus limited somewhere
20 in the middle of the column where both concentrations (of furfural and pentoses) are relatively low, so the risk of product loss due to formation of byproducts is minimized.

The process of the invention is further very energy efficient. This is in particular achieved by making use of vapour-recompression or heat-pump
25 assisted evaporation. Accordingly, in a preferred embodiment, the bottom part of the column is heated by condensing a compressed vapour on the hot side of the heat exchanger. Such condensing should be able to produce sufficient steam in the reaction column.

The compressed vapour fed to the hot side of the heat exchanger can be formed either by compressing the vapour product stream or a different stream.

In case the compressed vapour product is used for this purpose, the
5 process comprises the further step of compressing the vapour product stream recovered from the top of the column. The compressed vapour product stream is condensed on the hot side of the heat exchanger to produce the steam upflow in the column.

In case a vapour stream other than the vapour product stream is
10 used for condensing a compressed gas on the hot side of the heat exchanger, such a vapour stream is produced from a liquid stream by transferring heat from the vapour product stream to the liquid stream. Accordingly, the process of the invention may comprise the step of condensing the vapour product stream is conducted by bringing the vapour product stream in
15 thermal contact with a second liquid stream, thereby vaporizing the second liquid stream to form a second vapour stream that is subsequently compressed and condensed on the hot side of the heat exchanger to produce the steam upflow in the column.

The energy efficiency of the process of the invention is based
20 thereon that by using conventional heat recovery systems, the major part of the energy consumption in the process resides in the recompression of the vapour (either product or second vapour). Because of the system vapour-liquid equilibrium, the top and bottom temperatures of the column differ by only few Kelvin. For this reason the energy consumption due to the vapour
25 recompression can be minimal, and such to ensure an appropriate temperature difference between the hot (e.g. shell) and cold (e.g. tube) sides of the shell and tube heat exchanger. By virtue of such energy conservation measure, the external steam (energy) input is minimal, yet plentiful steam stripping may still be applied to the benefit of the overall furfural yields.
30 More in particular it is possible that the steam production in the bottom of

the column is fully provided for by the heat available in the said water and
furfural containing vapour product stream. The present invention
accordingly resides therein that the thermodynamic properties of the system
allow for a very efficient and economic production and separation process of
5 furfural from pentoses.

Pentoses and/or soluble pentosans used for this process are
preferably obtained from biomass or the residues of biomass conversion.
Soluble oligomers of pentoses (pentosans) are sometimes present together
with pentoses in liquors containing pentoses. The pentosans are generally
10 depolymerised rapidly under the conditions required for the production of
furfural from pentoses, in particular from xylose and arabinose.

The process can be performed with or without the use of an acidic
catalyst. It is preferred that an acidic catalyst system is present. This may
be a mineral or organic acid dissolved in the aqueous liquid downflow in
15 order to attain a pH lower than 3, preferably lower than 1.5. Suitable acids
are sulphuric acid, hydrochloric acid or phosphoric acid. However, it is also
possible that the interior of the column or the heat exchanger contains an
acidic material on the surface thereof, in particular, those parts of the
interior of the column or heat exchanger that are in contact with the
20 pentose/pentosans containing aqueous stream. This material may then be
applied to the trays, tube-walls or packing material. Suitable acidic
materials to be used herein are acidic zeolites; microporous and mesoporous
niobium silicalites; micro-mesoporous sulfonic acids; layered titanates,
niobates and titanoniobates; delaminated aluminosilicates; cesium salts of
25 12-tungstophosphoric acid and mesoporous silica-supported 12-
tungstophosphoric acid; bulk and mesostructured sulfated zirconia;
nafion; and a combination of different acid and basic solid catalysts and the
like.

The liquid in the column may be recycled. Typically, the liquid
30 upflow is fed from the top of the reaction column back to the bottom of the

reaction column via the heat exchanger. The liquid may be treated before feeding it back to the reaction column or heat exchanger.

In case of the use of an acidic material dissolved in the aqueous liquid upflow, the acidic components are preferably recycled to the bottom of the column.

According to a further preferred embodiment, the aqueous phase additionally contains a dissolved salt, namely an alkali, earth alkali or ammonium halides, such as common sea salt, NaCl, KCl, CaCl₂, NH₄Cl, and the equivalent bromides and iodides.

This embodiment may be combined with the use of dissolved acidic material or solid acidic materials anchored to the column or packing material.

Thus, the recycle stream optionally contains the catalyst and it might contain some electrolyte (salt) in order to optimize the catalytic conversion of pentoses into furfural besides enhancing the separation of furfural.

During the vapour-liquid contact, the pentoses are converted to furfural which at least partly transfers to the vapour phase. The vapour phase obtained at the top of the column is condensed, for example in the reboiler system of the column. The furfural containing condensate can then be used as such in further processes, as concentrated furfural solution, or the furfural may be recovered from it, preferably by further distillation using a column equipped with recompression and condensation of the vapour product. This column may be a distillation column which is heated using a reboiler.

As indicated above, the pentoses containing feed stream is preferably biomass or biomass derived, for example as secondary product from the paper industry, cellulosic ethanol refineries, sugar factories or anywhere it may become available in suitable amounts. It may also be produced in dedicated facilities where the pentosans are separated from raw

biomass material, such as woody biomass, agricultural residues or similar, using different existing technologies, such as steam explosion, dilute acid, alkaline, or hot water hydrolysis, organosolv, supercritical water hydrolysis, different pulping technologies and the like, or a combination these.

5 The temperature and pressure conditions of the process may vary between relatively wide limits, and depending on the optimization of economic factors. It is preferred to carry out the reaction at temperatures between 100 and 300°C, preferably between 150 and 250°C. The reaction pressure depends on the temperature of choice for the reaction, and will be
10 very similar that of pure saturated water at the same temperature.

 The concentration of pentoses in the feed stream is not critical, but it should be such to result in a pentoses concentration inside the reactor(s) preferably below 10 wt.% in water solution, more in particular between 1 and 4 wt.%. The concentration can easily be maintained at this
15 level by the selection of the amount of recycle or simply by dilution.

 The reaction for producing furfural may fully take place in the reaction column and heat-exchanger or only partly. In the latter case, a pre-reaction step may first be conducted, wherein an aqueous containing feed stream containing both furfural and pentose and/or pentosan is produced,
20 for example by heating an aqueous solution of pentoses and/or water soluble pentosans.

 Preferably, the aqueous pentose solution is fed to the bottom of the reaction column via the heat exchanger. For example, in case of a shell and tube heat exchanger, the aqueous pentose solution will be fed to the bottom
25 of the reaction column via the tubes of the shell and tube heat exchanger. Accordingly, no separate inlet is required for feeding liquid to the reaction column. Also, when using a reboiler of the shell and tube type, it is no longer needed to use a bottoms liquid, but the aqueous pentose solution can be directly fed to the reboiler.

The reaction column used in the process may be any type of column, provided that it allows for a liquid upflow. Accordingly, it is not desirable to use conventional tray columns which are used in traditional distillation columns. An example of a suitable reaction column is a packed column. In a preferred embodiment, the heat exchanger is a shell and tube heat exchanger, which was found to be very suitable for use as the heat exchanger in the present invention. The heat exchanger used in the invention may be part of a reboiler, preferably a vertical reboiler, more preferably a vertical thermosyphon reboiler.

In a particular preferred embodiment, the heat exchanger and the reaction column are part of a column reactor. The reaction column is preferably located on top of said exchanger. In case of a shell and tube heat exchanger, the tube exits of the shell and tube heat exchanger are preferably located at the bottom part of the reaction column. Preferably, a column reactor according to the second aspect of the invention is used, which comprises both the reaction column and the shell and tube heat exchanger.

In a second aspect, the invention is directed to a column reactor and to an apparatus for producing furfural from pentoses and/or water soluble pentosans comprising such a column reactor. The column reactor was specifically designed for the process of the invention, since this process can not simply be conducted in a traditional distillation column due to the required liquid upflow.

Accordingly, the column reactor of the invention comprises

- a reaction column (301), located at the top part of the reactor; and
- a shell and tube heat exchanger (302) located at the bottom part of the reactor, which exchanger comprises a shell and a tube bundle, wherein the tube exits of the tube bundle (303) are located at the bottom part of the reaction column; and

- a reactor inlet (304) located at the bottom part of the reactor and connected to the tube inlets of the tube bundle, such that liquid can enter the bottom part of the reaction column via the tubes of the heat exchanger;

- a first reactor outlet (305) for vapour to exit the column reactor
5 located at the top part of the reaction column; and

- a second reactor outlet (306) for liquid to exit the column reactor located at the top part of the reaction column.

The shell and tube heat exchanger further comprises a shell inlet (307) for the heating medium to enter the exchanger and a shell outlet (308)
10 for heating medium to exit the exchanger. The heating medium is preferably steam.

The reaction column may be any type of column, provided that it allows for a liquid upflow. Accordingly, it is not desirable to use conventional tray columns which are used in traditional distillation
15 columns. An example of a suitable reaction column is a packed column.

The reaction column is typically located on top of the heat exchanger. In such a case, the top of the heat exchanger (and in particular of the tube bundle) may form the bottom of the reaction column.

In a preferred embodiment, the tube exits of the tube bundle are
20 located at the bottom part of the reaction column. The exits of the tubes of the tube bundle of said heat exchanger may for example form holes in the bottom of the reaction column. For example, a tube sheet with holes may at the same time form the top of the heat exchanger and the bottom of the reaction column. Steam and/or liquid can be provided through these holes to
25 the reaction column.

The reaction column may further comprise a packing material (309) located above the tube bundle of the heat exchanger for enhancing vapour-liquid mass transfer between the liquid upflow and the steam upflow.

The column reactor of the invention may further comprise a solid catalyst. For example, the interior of the column may comprise a coating or layer of a solid catalyst, *e.g.* present on the inner wall of the column, on the inner tube walls of the heat-exchanger or on the packing material if present.

5 The solid catalyst is preferably an acidic catalyst as described above for the process of the invention.

The apparatus of the invention comprises a column reactor as described above. In addition, the apparatus may comprise a compressor. The outlet of the compressor is connected to the shell inlet of the shell and tube
10 heat exchanger. Thus, compressed vapour can be used to heat the liquid entering the shell and tube heat exchanger.

In one embodiment, the inlet of the compressor is connected to the first reactor outlet, in order to compress the vapour exiting said outlet.

In a more preferred embodiment however, the inlet of the
15 compressor is connected to a second heat-exchanger, which brings the vapour stream coming from the first reactor outlet in thermal contact with a second stream. The latter configuration makes it possible that a stream other than the vapour product stream (*viz.* the second stream) can be compressed and used for heating in the shell side of the shell and tube heat
20 exchanger. The second stream can enter the second heat-exchanger, wherein it is heated by thermal contact with the vapour product stream to a steam, which is compressed and used in the shell and tube heat exchanger. Although more capital intensive, such a configuration has the advantage of reducing the chance of product contamination (from compressor lube oils)
25 and allowing the product to condensate at a somewhat lower temperature, thus reducing undesirable reactions that may result in loss of product.

The invention will be further illustrated by the following example.

Example 1:

The concentrations of furfural and pentose in the liquid and furfural in the vapour were estimated based on the inventors' experience from lab experiments on reaction kinetics and yields, and from reasonable engineering assumptions. These estimates are depicted in figure 4 and support the theory that a significant amount of product loss may occur as a result of undesirable reactions involving furfural, pentose and possible reaction intermediates.

CLAIMS

1. Process for the production of furfural from pentoses and/or water soluble pentosans, wherein the process comprises the steps of
 - feeding an aqueous pentose solution containing one or more pentoses or soluble pentosans to the bottom of a reaction column to produce an aqueous
 - 5 liquid upflow; and
 - heating the bottom part of the column using a heat exchanger to produce a steam upflow in the column; and
 - recovering a vapour product stream containing water and furfural from the top of the column; and
 - 10 - condensing the vapour product stream, thereby obtaining an aqueous furfural containing product solution as the condensate.
2. Process according to claim 1, wherein the bottom part of the column is heated by condensing a compressed vapour on the hot side of the heat exchanger, wherein the heat exchanger is preferably a shell and tube
- 15 heat exchanger.
3. Process according to claim 2, wherein the step of condensing the vapour product stream is conducted by bringing the vapour product stream in thermal contact with a second liquid stream, thereby vaporizing the second liquid stream to form a second vapour stream that is subsequently
- 20 compressed and condensed on the shell side of the shell and tube heat exchanger to produce the steam upflow in the column.
4. Process according to claim 2, further comprising the step of
 - compressing the vapour product stream recovered from the top of the column prior to condensing; and
 - 25 wherein said condensing is conducted on the shell side of the shell and tube heat exchanger to produce the steam upflow in the column.
5. Process according to any of the previous claims, wherein the aqueous pentose solution is fed to the bottom of the reaction column via the tubes of the shell and tube heat exchanger.

6. Process according to any of the previous claims, wherein the shell and tube heat exchanger and the reaction column are part of a column reactor, wherein said column is located on top of said exchanger, and wherein the tube exits of said heat exchanger are located at the bottom part of the reaction column
7. Process according to any of the previous claims, wherein the liquid in the reaction column further comprises at least one salt, such as an alkali, earth alkaline or ammonium halide.
8. Process according to any of the previous claims, wherein the production of furfural occurs under acidic conditions.
9. Process according to any of the previous claims, wherein at least one acidic material is present in the liquid upflow in an amount of at most 0.5 N, preferably a mineral acid such as sulphuric acid, phosphoric acid or hydrochloric acid.
10. An apparatus for producing furfural from pentoses and/or water soluble pentosans comprising a column reactor, which reactor comprises
- a reaction column (301), located at the top part of the reactor; and
 - a shell and tube heat exchanger (302) located at the bottom part of the reactor, which exchanger comprises a shell and a tube bundle (303), wherein the tube exits of the tube bundle are located at the bottom part of the reaction column; and
 - a reactor inlet (304) located at the bottom part of the reactor and connected to the tube inlets of the tube bundle, such that liquid can enter the bottom part of the reaction column via the tubes of the heat exchanger;
 - a first reactor outlet (305) for vapour to exit the column reactor located at the top part of the reaction column; and
 - a second reactor outlet (306) for liquid to exit the column reactor located at the top part of the reaction column.
11. An apparatus according to claim 10, wherein the reaction column further comprises a packing material (309).

12. An apparatus according to claim 10 or 11, wherein the packing material, the inner column wall or the inner tube walls of the heat-exchanger tubes are coated with a solid catalyst, preferably a solid acidic catalyst.

5 13. An apparatus according to any of claims 10-12, wherein the apparatus further comprises a compressor, wherein the outlet of the compressor is connected to the shell inlet of the shell and tube heat exchanger.

10 14. An apparatus according to claim 13, wherein the inlet of the compressor is connected to the outlet of a second heat exchanger, which second heat exchanger brings the vapour stream coming from the first reactor outlet in thermal contact with a second stream.

15. An apparatus according to any of claims 10-14, wherein the upper part of the tube bundle forms the bottom part of the reaction column.

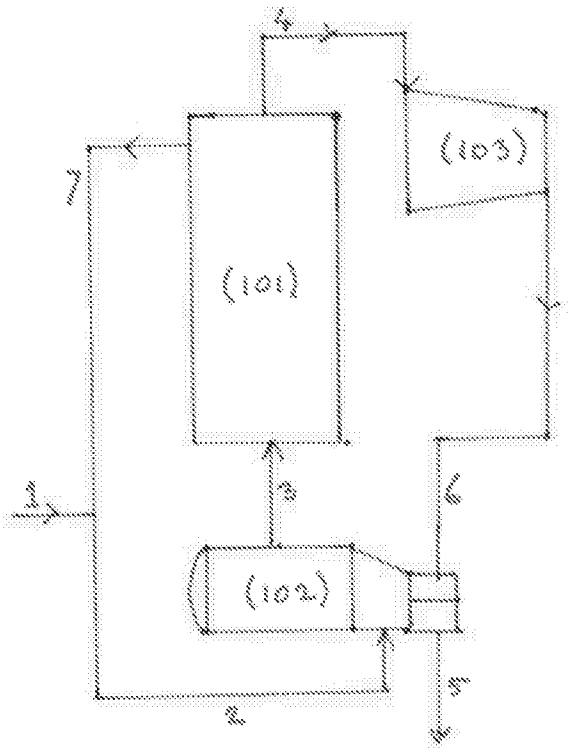


Fig. 1

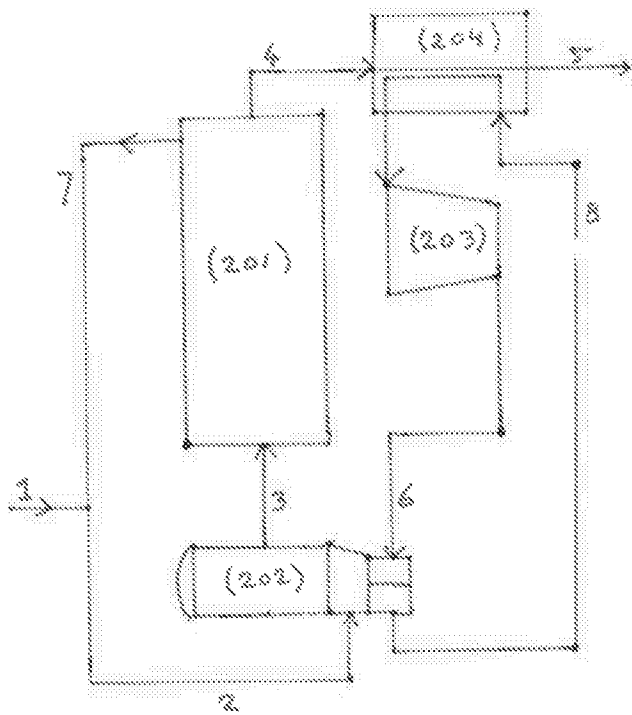


Fig. 2

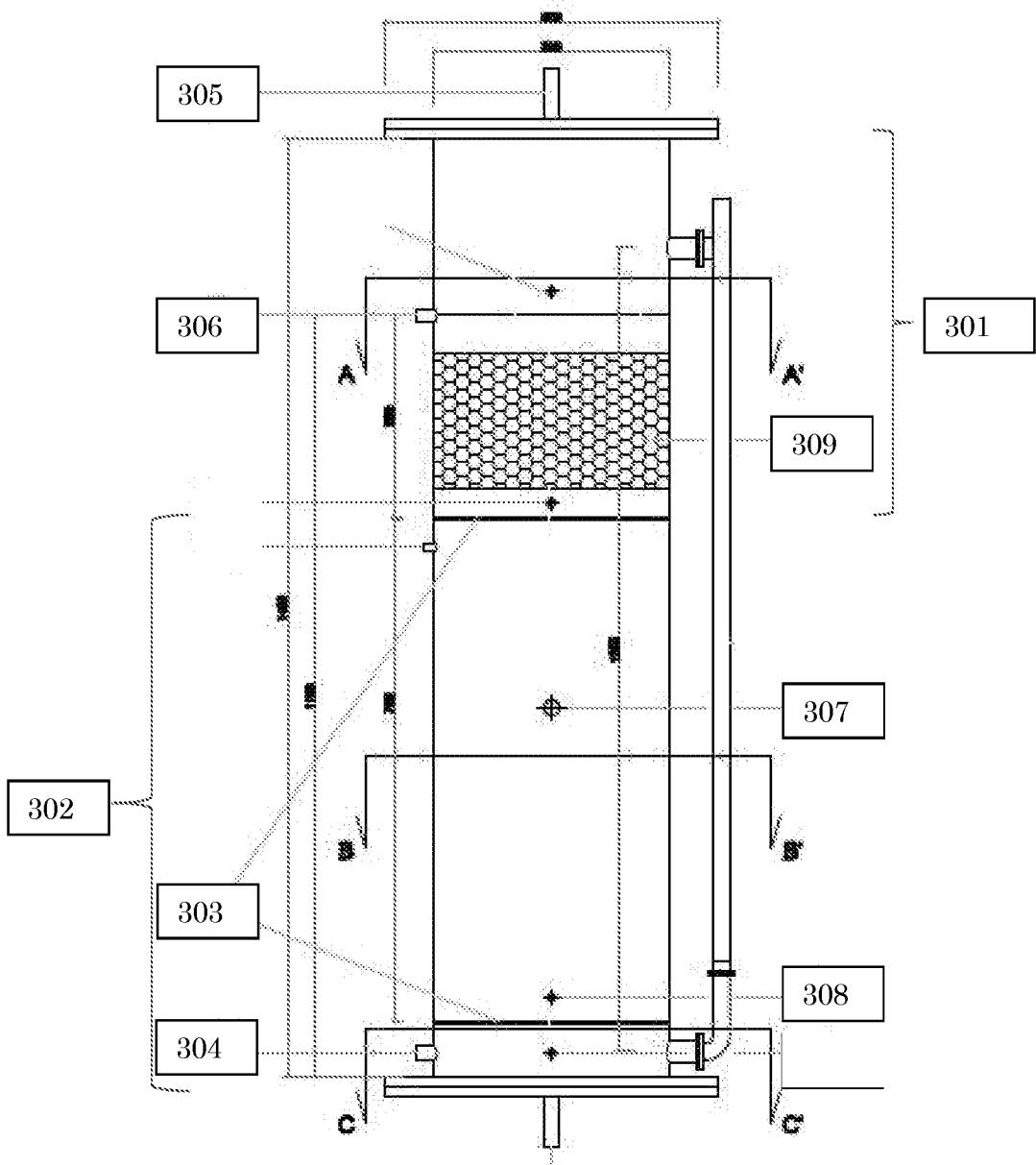


Fig. 3a

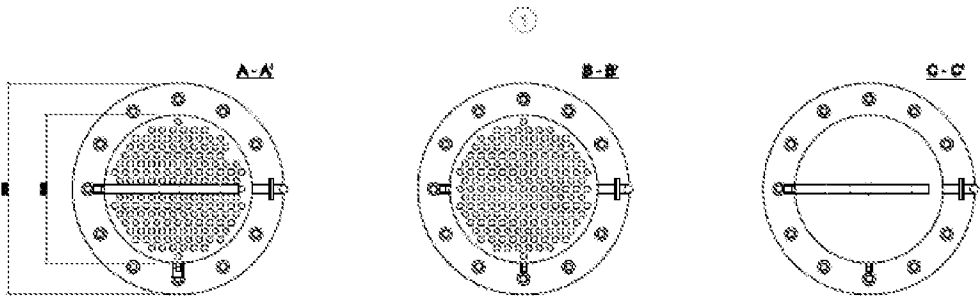


Fig. 3b

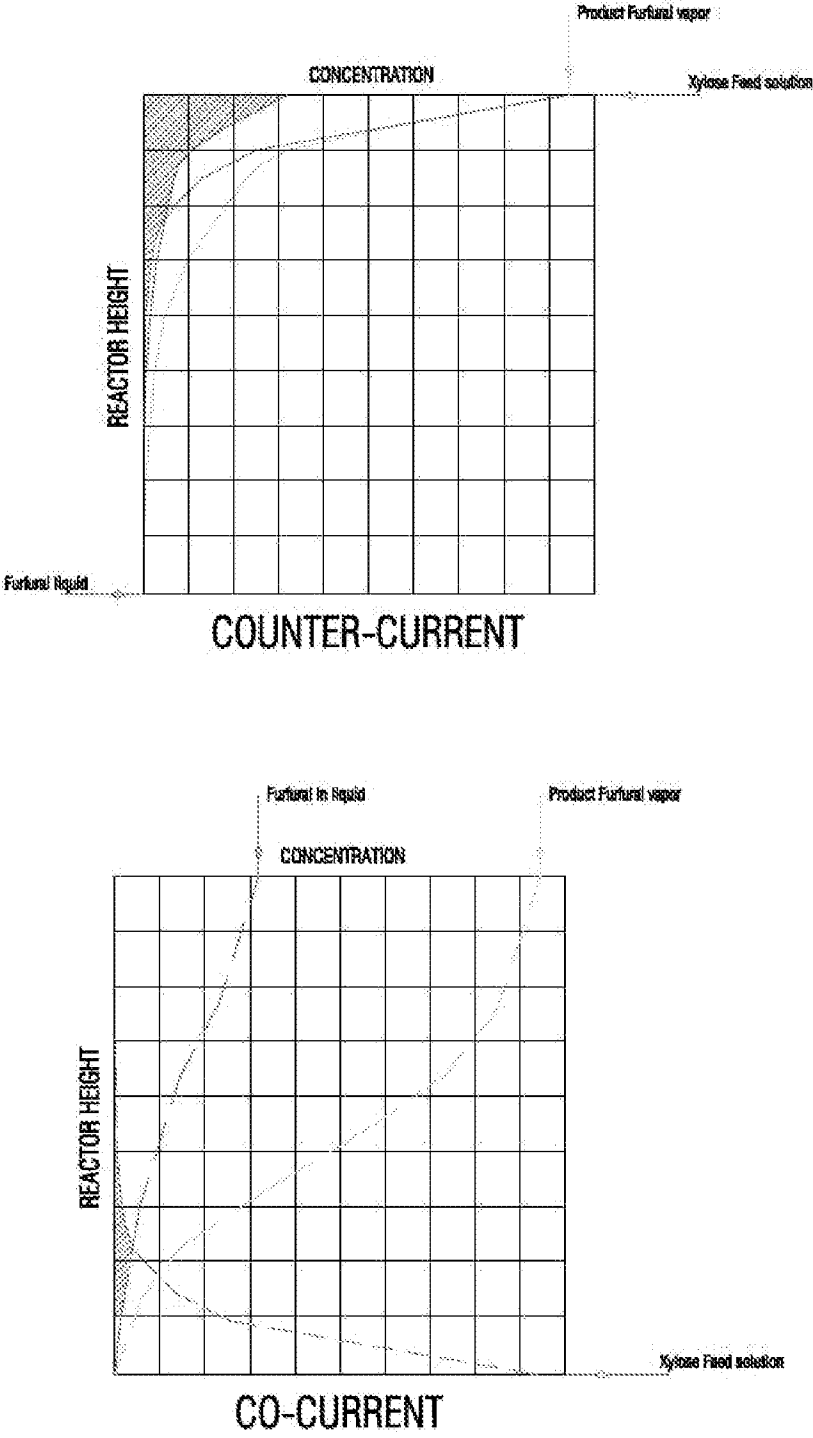


Fig. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2015/050341A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D307/50 B01J8/06
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)
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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, CHEM ABS Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2012/057625 A2 (UNIV DELFT TECH [NL]; DE JONG WIEBREN [NL]; MARCOTULLIO GIANLUCA [NL]) 3 May 2012 (2012-05-03) cited in the application the whole document -----	1-15



Further documents are listed in the continuation of Box C.



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Date of the actual completion of the international search

26 August 2015

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2012057625 A2	03-05-2012	AU 2011321090 A1	23-05-2013
		EP 2632911 A2	04-09-2013
		NL 2005588 C	01-05-2012
		US 2012108829 A1	03-05-2012
		WO 2012057625 A2	03-05-2012
