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(54) Benævnelse: **Fremgangsmåde til behandling af procesvand**

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Description

[0001] The present invention relates to a method for the treatment of process water, particularly in advance of extraction of the reaction products.

[0002] The state of the art knows several methods for the treatment of process water, such as DE 10 2012 002 590 A1 of the same applicant. It is proposed there to extract organic substances from process water produced by a hydrothermal carbonisation process by means of a two-stage membrane filtration in order to recycle them back into the reaction process in order to increase its efficiency.

[0003] DE 10 2011 053 034 A1 of the same applicant discloses a method for obtaining furfurals in which hydroxymethyl furfural is separated by means of a separation process and ejected from the process.

[0004] From DE 20 2012 100 129 U1 of the same applicant, it is known that biochar is separated from the process water of a hydrothermal

[0005] carbonization reaction, wherein the filtration process is carried out by means of a filter device.

[0006] US Pat. No. 5,635,071 A1 provides for the removal of carboxylic acid using a membrane filter.

[0007] Within the scope of hydrothermal carbonization, biomass is carbonized in a reaction container, with the addition of steam, in a temperature range of about 150-230°C and at an elevated pressure of about 4-28 bar. Aside from the biochar that results in this way, other products also occur during this process, such as particularly the basis chemicals 5-hydroxymethyl furfural, furfural, and

levulinic acid. These are extracted from the process water during a subsequent step, wherein the process water passes through an extraction column for this purpose.

[0008] Aside from the actually desired carbonization reaction, however, many different secondary reactions occur, so that aside from the desired products, a number of humic substances and oligomers are formed. In this connection, oligomers are small, branched chains composed of individual monomers of the products. Because of their method of formation, they have a great similarity with the products in terms of their physical and chemical properties, and cannot be separated from the products during the subsequent process steps, or can be separated only with difficulty, and thereby lead to a reduction in product purity. Just like the humic substances that are also formed, the oligomers therefore represent impurities in the extraction, wherein clearly more humic substances occur. The humic substances can occur both in dissolved and non-dissolved form, wherein the non-dissolved part leads to reduction in throughput and contaminants as the result of deposition during cooling in the heat exchanger, so that in part, the production process of the products must be interrupted for cleaning of the heat exchanger. The dissolved portions, in contrast, disrupt the further process steps of product isolation, in other words, in particular, extraction of the products. They deposit on the walls and separation apparatuses of the extraction columns and therefore require a high level of cleaning effort, in order to keep the systems in operation.

[0009] Against this background, the present invention is based on the object of keeping the cleaning effort for the

extraction columns low and, at the same time, of improving product purity and thereby increasing the quality of the product, in other words of the 5-hydroxymethyl furfural, the furfural, and the levulinic acid.

[00010] This is accomplished by means of a method for treatment of process water of a hydrothermal carbonization process in accordance with the features of claim 1. Further practical embodiments of such a method can be derived from the dependent claims.

[00011] According to the invention, for this purpose the process water is passed through a filter cascade, which has multiple filtration stages, before entry into the extraction column. In each filtration stage, the components in the process water, of which the size of the individual particles exceeds the permeability of the filtration stage, in each instance, are eliminated. Thus, the separation means in the first filtration stage are selected so that essentially the impurities, in other words the humic substances and the oligomers, are retained as a retentate. The products 5-hydroxymethyl furfural, furfural, and levulinic acid continue to be contained in the permeate that represents the main stream, along with the educts such as fructose or glucose, for example. This particularly holds true for liquid educts. To the extent that solid educts, such as topinambur or wood chips, for example, are used, these remain in the reactor.

[00012] In a second filtration stage, to which the permeate of the first filtration stage is passed as a feed stream, the separation means are once again selected in such a manner that the educts, in other words essentially fructose and glucose, are retained as a second retentate, while a

second permeate more or less now contains only the products 5-hydroxymethyl furfural, furfural, and levulinic acid, as well as all the substances that once again are smaller than these.

[00013] By means of this method of procedure, multiple problems are solved at the same time. The humic substances that dirty the extraction columns and therefore lead to great effort and expenditure are eliminated by the first filtration. Likewise, the oligomers, which would contaminate the product, are eliminated within the scope of the first filtration. The fructose and/or glucose separated out in the second step can be passed back into the method, in other words placed in the reactor, and there can improve the yield in a further pass.

[00014] With some advantage, further separation of the second permeate can possibly take place by means of further filtration stages, so that filtration taking place one stage after another, using a separation means, the permeability of which lies once just above the size of the products and once just below the size of the products, precise filtration of individual products can take place. In this connection, the molecule size is the deciding factor, in each instance.

[00015] The same method of procedure can likewise be followed for the second retentate. Within this filtration cascade that has been shown, the last separation stage has the task of increasing the concentration of the products or educts by means of carrying away reaction water. By means of this step, the subsequent extraction can be carried out more efficiently. The permeates formed are particularly suitable for being passed back to an earlier filtration

stage within the cascade, so that in these, no additional substances, such as dissolved salts, organic substances or bacteria, for example, are introduced into the system and thereby increase the degree of purity once again.

[00016] Preferably, membrane filters are provided as separation means in the individual filtration stages; particularly preferably, these are solution/diffusion membranes and/or ion-selective membranes such as anion exchanger membranes or cation exchanger membranes, because in this way, the yield can be improved, with simultaneous reduction of operating substances and ancillary substances.

[00017] Furthermore, it has been proven to be practical to keep the inflow of process water and/or permeate to a filtration stage uniform, and thereby to ensure that the inflow more or less corresponds to the outflow.

[00018] Since the process water, as it is directly taken from the reactor of the hydrothermal carbonization, also contains the biochar that has formed, it is furthermore practical to pass the process water to a separate solid/liquid filtration stage before entry into the first filtration stage. For this purpose, surface or depth filtration, particularly preferably membrane filtration, is carried out here, as well.

[00019] The invention described above will be explained in greater detail below, using an exemplary embodiment.

The drawings show as follows:

[00020]

Fig. 1 shows a simple filter cascade having two filter stages, in a schematic representation, and

Fig. 2 shows an expanded filter cascade having three filter stages, in a schematic representation.

[00021] Fig. 1 shows a simple filter cascade with which incoming process water 1 from the hydrothermal carbonization process is supposed to be pretreated before entry into the extraction column. At the point in time being observed, the process water 1 has already passed through a solid/liquid filtration, which is not of any great interest here and therefore has not been shown in the drawing, and enters into a first filtration stage 2 in this situation. This is a membrane filtration stage, the permeability of which is structured in such a manner that impurities 3 such as humic substances or oligomers are retained in the first filtration stage 2 as a retentate, while products 7 and educts 6, in other words 5-hydroxymethyl furfural, furfural, and levulinic acid, on the one hand, and sugar, sugar derivatives, and, in this connection, in particular, fructose, on the other hand, pass through the first filtration stage 2 in a first permeate 4. The impurities 3 are conducted away from the first filtration stage 2 and passed to further use or disposal. The first permeate 4, which contains the educts 6 and the products 7, is then passed to a second filtration

stage 5, which also represents a membrane filtration stage. The permeability of this second filtration stage 5, however, is selected in such a manner that the educts 6 are retained, while the products 7 can once again pass through the second filtration stage 5. In this case, the educts 6 are retained as a retentate and passed back into the process of hydrothermal carbonization, for example. The second permeate with the products 7 can now be passed to the extraction column.

[00022] Fig. 2 shows an alternative to the filter cascade shown in Fig. 1, in which not only the second retentate 8 but also the second permeate 9 are passed to a renewed further filtration stage 11. By means of the renewed filtration, up-concentration of the desired substances takes place, so that the subsequent processes take place more effectively, and therefore the extraction columns can work more effectively with regard to the products 7. In this connection, the further permeates 10 from the further filtration stages 11 are furthermore passed to the earlier filtration stages, in other words the first filtration stage 2 and the second filtration stage 5, and thereby bring with them a washing-out effect as support for the separation process by means of diafiltration.

[00023] Therefore, a method for treatment of process water of a hydrothermal carbonization process has been described above, in the course of which method the process water that occurs in the hydrothermal carbonization process is filtered in such a manner that greater product purity and, at the same time, a lower degree of contamination occurs for the systems in question, and thereby the efficiency of the method is clearly improved.

P A T E N T K R A V

1. Fremgangsmåde til behandling af procesvand (1) fra en hydrotermisk karboniseringsproces, hvor procesvandet (1) i et første filtreringstrin (2) ved hjælp af et membranfilter deles i et første retentat, der i det væsentlige indeholder huminstoffer og/eller oligomerer, og et første permeat (4), der i det væsentlige indeholder produkter (7), nemlig 5-hydroxymethylfurfural og/eller furfural og/eller levulinsyre, og edukter (6), nemlig glukose og/eller fruktose, og det første permeat (4) tilføres til et andet filtreringstrin (5) ved hjælp af et membranfilter, hvori det første permeat (4) deles i et andet retentat (8), der i det væsentlige indeholder glukose og/eller fruktose, og et andet permeat (9), der i det væsentlige indeholder 5-hydroxymethylfurfural og/eller furfural og/eller levulinsyre, hvorefter det andet permeat (9) tilføres til et ekstraktionstrin til ekstraktion af produkterne (7) ved hjælp af en ekstraktionskolonne.

2. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** det andet permeat (9) forud for tilførslen til ekstraktionstrinet tilføres til mindst et yderligere filtreringstrin (11), hvori det andet permeat (9) deles i yderligere permeater (10), der indeholder forskellige enkeltprodukter, og yderligere retentater.

3. Fremgangsmåde ifølge et af kravene 1 eller 2, **kendetegnet ved, at** det andet retentat (8) opkoncentreres i mindst et yderligere filtreringstrin (11).

4. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** permeaterne (10) fra det sidste filtreringstrin

eller de sidste filtreringstrin (11) tilføres til tidligere filtreringstrin (2, 5) som tilstrømning.

5. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** efter hinanden følgende filtreringstrin adskiller sig ved, at de tilbageholder molekyler af tiltagende mindre størrelse.

6. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** tilstrømningen af procesvand (1) og/eller permeat (4, 9, 10) til et filtreringstrin (2, 5, 11) sker ensartet.

7. Fremgangsmåde ifølge krav 6, **kendetegnet ved, at** tilstrømningen af procesvand (1) og/eller permeat (4, 9, 10) til et filtreringstrin (2, 5, 11) er indstillet således, at bortstrømningsmængden højst svarer til tilstrømningsmængden.

8. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** procesvandet (1) forud for indstrømning til det første filtreringstrin (2) tilføres til et separat fast/flydende filtreringstrin.

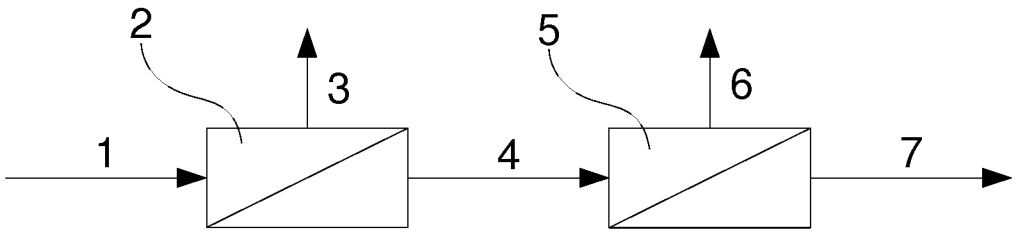

Fig. 1

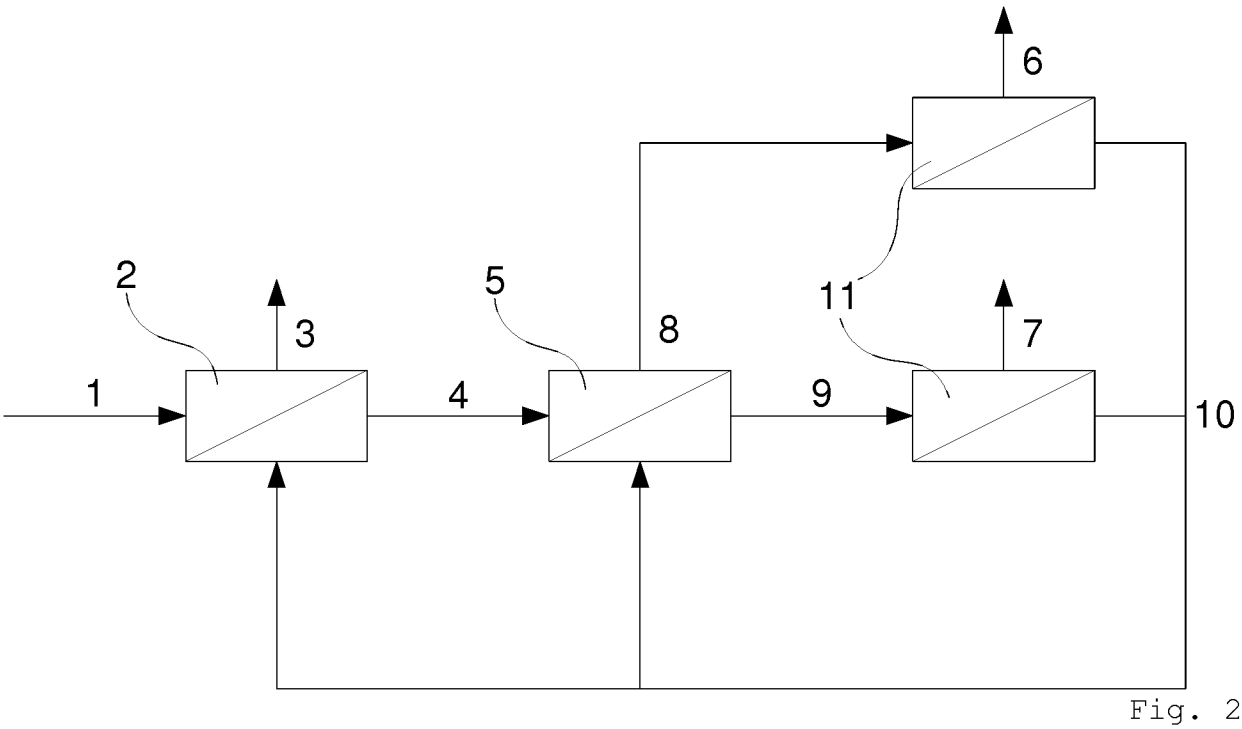

Fig. 2