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(71) Applicant (for all designated States except US): UPM-KYMMENE CORPORATION [FI/FI]; Eteläesplanadi 2, FI-00130 Helsinki (FI).

(72) Inventors; and

(75) Inventors/Applicants (for US only): RISTOLAINEN, Matti [FI/FI]; Upseeritie 14 B 9, FI-53900 Lappeenranta (FI). NUORTILA-JOKINEN, Jutta [FI/FI]; Iivisniemenaukio 4 B 20, FI-02260 Espoo (FI). HASSINEN, Esa [FI/FI]; Vihnekatu 2, FI-53500 Lappeenranta (FI). ESKELINEN, Kati [FI/FI]; Tuulikinkuja 5, FI-55100 Imatra (FI).

(74) Agent: PAPULA OY; Mechelininkatu 1 a, FI-00180 Helsinki (FI).

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[Continued on next page]

(54) Title: METHOD AND APPARATUS FOR MANUFACTURING A HYDROXYCARBOXYLIC ACID PRODUCT AND USE OF BLEACHING FILTRATE

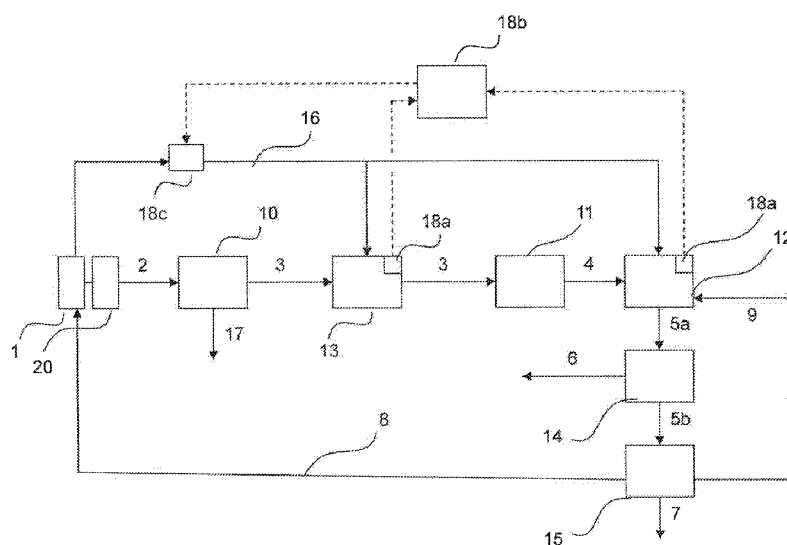


Fig. 1

(57) Abstract: The invention relates to a method and an apparatus for manufacturing a hydroxycarboxylic acid product from ligno-cellulose-based raw material. According to the invention, a first effluent (2) used as a raw material is concentrated to provide a concentrate (3), the concentrate (3) is treated by a hydrolysis (11) to form saccharides (4), the saccharides (4) are fermented (12) to form hydroxycarboxylic acid, and the pH of the fermentation (12) is controlled by using a second effluent (16), for forming a hydroxycarboxylic acid product. Further, the invention relates to use of a bleaching filtrate.



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**METHOD AND APPARATUS FOR MANUFACTURING A
HYDROXYCARBOXYLIC ACID PRODUCT AND USE OF BLEACHING
FILTRATE**

5 FIELD OF THE INVENTION

The invention relates to the method as defined in the preamble of claim 1 and to the apparatus as defined in the preamble of claim 16 for manufacturing a hydroxycarboxylic acid product from lignocellulose-based material. Further, the invention relates to
10 the use of a bleaching filtrate as defined in the claim 27.

BACKGROUND OF THE INVENTION

15 Hydroxycarboxylic acid based products, e.g. lactic acid, are manufactured from different kinds of lignocellulose-based raw stock, e.g. from waste waters, residue flows and sludges derived from paper and/or pulp mill. The waste waters contain organic material such as fibers and traces of bleaching agents.
20 The process of hydroxycarboxylic acid production is usually based on enzymatic hydrolysis and fermentation. The produced hydroxycarboxylic acid is separated for example by crystallization.

25 From JP 59014792 is known a method for preparing citric acid. The citric acid is prepared by culturing micro-organism capable of producing citric acid, in a medium containing a sugar obtained from the waste liquid of SP pulp as a carbon source. From JP
30 59115795 is known a method in which the sulfite pulp waste liquid is concentrated with an ultrafilter and resulting liquid is further concentrated by a vacuum evaporator and is then burned in a recovery boiler. From WO 9919290 is known a process for the production
35 of lactic acid products from mixture containing free

lactic acid and dissolved lactate salt. Preferred mix-
tures for processing are obtained from fermentation
broths, preferably from fermentation processes con-
ducted at a pH of 4.8 or lower. From WO 00/56693 is
5 known a method for purificating lactic acid by distil-
lation and crystallization.

OBJECTIVE OF THE INVENTION

The objective of the invention is to dis-
10 close a new type of a method and apparatus for manu-
facturing a hydroxycarboxylic acid product. Further,
an objective of the invention is to disclose the use
of a bleaching filtrate as a pH-controlling agent.

SUMMARY OF THE INVENTION

The method for manufacturing a hydroxycarbox-
ylic acid product according to the present invention
is characterized by what is presented in claim 1.

The apparatus for manufacturing a hydroxycar-
20 boxylic acid product according to the present inven-
tion is characterized by what is presented in claim
16.

The use of a bleaching filtrate according to
the present invention is characterized by what is pre-
25 sented in claim 27.

BRIEF DESCRIPTION OF THE FIGURES

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

Fig. 1 is a flow chart illustration of a
35 method and an apparatus according to one embodiment of
the present invention, and

Fig. 2 is a flow chart illustration of a method and an apparatus according to another embodiment of the present invention.

5 DETAILED DESCRIPTION OF THE INVENTION

The invention is based on a method for manufacturing a hydroxycarboxylic acid product 7 from lignocellulose-based raw material. According to the invention a first effluent 2 used as a raw material is concentrated 10 to provide a concentrate 3, the concentrate is treated by a hydrolysis 11 to form saccharides, preferably monosaccharides, the saccharides 4 are fermented 12 to form hydroxycarboxylic acid, and the pH of the fermentation 12 is controlled 18 a-c by using a second effluent 16, and a hydroxycarboxylic acid product 7 is formed of hydroxycarboxylic acid.

Further, the invention is based on an apparatus for manufacturing a hydroxycarboxylic acid product from lignocellulose-based raw material. According to the invention, the apparatus for forming hydroxycarboxylic acid product includes an effluent feeding means 20 for feeding a first effluent 2 used as a raw material to the apparatus; a first concentration device 10 for concentrating the first effluent to provide a concentrate 3; a hydrolysis and fermentation unit 11, 12, 21 for treating the concentrate 3 by hydrolysis 11 to form saccharides 4 and for fermenting 12 the saccharides 4 to form hydroxycarboxylic acid; and a pH controlling means 18a-c for controlling the pH of the fermentation 12 by using a second effluent 16.

Further, the invention is based on use of a bleaching filtrate in controlling the pH of hydrolysis and/or fermentation of a pulp mill effluent in hydroxycarboxylic acid product manufacturing.

Lignocellulose means in this connection a material formed from cellulose, hemicellulose and lignin. Lignocellulose-based material means in this connection any material containing cellulose and/or hemicellulose, which may also contain, in addition to cellulose and hemicellulose, lignin, starch and/or other substances.

In this connection, the term "effluent" means any effluent selected from the group of pulp mill effluent, paper mill effluent, saw mill effluent, food manufacturing effluent, brewing industry effluent and their combinations. The effluent comprises alkaline and/or acidic waste waters, filtrates and residual waters of the process. The effluent contains, at least in some quantity, the lignocellulosic material described above. The effluent can include one or more than one component.

In one embodiment the first effluent is coming from a pulp mill. In one embodiment the first effluent is a waste water, waste sludge or residue flow from the pulp mill. In one embodiment the first effluent is a waste water. In one embodiment the first effluent can include alkaline and/or acid components, e.g. a bleaching filtrate, and/or any residue effluent which comes from the pulp mill. In one embodiment the first effluent is an alkaline bleaching filtrate. The first effluent, used as raw stock in the process according to the invention, can also contain, in addition the effluent, other substances.

In one embodiment the second effluent is coming from a pulp mill. In one embodiment the second effluent can be an alkaline and/or acid effluent, e.g. a bleaching filtrate, which comes from the pulp mill.

In one embodiment the first effluent is substantially same material than the second effluent. In

one embodiment the first effluent is partly same material than the second effluent.

A saccharide means in this connection any fraction mainly based on monosaccharides. The saccharides
5 may contain disaccharides and/or oligosaccharides. In one preferred embodiment, the disaccharides and oligosaccharides are mainly disintegrated to monosaccharides in the process according to the invention.

In one embodiment the pH is controlled during
10 the fermentation 12 by the second effluent 16. In one embodiment of the invention the pH is controlled, and preferably adjusted, during the fermentation by the second effluent, preferably alkaline and/or acid bleaching filtrate from the pulp mill. In one embodi-
15 ment the pH is controlled by the alkaline bleaching filtrate from the pulp mill.

In one embodiment, the bacteria survive at pH 4 - 8 in the fermentation, more preferably at pH 5 - 7. In one embodiment the temperature in the fermenta-
20 tion is set between 30 and 80°C. In one embodiment, yeast, bacteria, microbes, nutrients or their mixtures are fed to the suspension in connection with fermentation to promote the fermentation. In one embodiment of the invention, at least one enzyme is added to the sus-
25 pension in connection with fermentation.

In one embodiment the pH of the first effluent is controlled, preferably for neutralizing the acidic substances of the first effluent, before hydrolysis 11 and/or fermentation 12 by the second effluent 16. In
30 one embodiment the pH of the first effluent is adjusted suitable for enzymatic hydrolysis and/or fermentation by using a second effluent with alkaline or acid composition, e.g. by an effluent from the pulp mill such as a bleaching filtrate from the pulp mill.

35 The use of the alkaline bleaching filtrate as the second effluent in the pH controlling gives the ad-

vantage that the hydrogen peroxide residues in the filtrate kill all the unwanted bacteria in the first effluent. In one embodiment the killing the unwanted bacteria requires sufficient dwelling time. In the enzymatic hydrolysis, the new hydrolyzing bacteria are added and there are no competing bacteria, since they have been destroyed by the hydrogen peroxide in the second effluent. In addition, the alkaline bleach filtrate contains a lot of carbohydrates, which increase the yield of fermentation.

In one embodiment of the invention, water 17 is removed 10 from the first effluent 2, e.g. from the first pulp mill effluent, to provide a concentrate 3. In one embodiment water is removed from the first effluent to provide a concentrate so as to have in the first effluent a percentage of solids of approximately 1 to 2% after removal of water.

In one embodiment of the invention the first effluent 2, e.g. the first pulp mill effluent, is filtered 10 to provide a concentrate 3. In one embodiment the first effluent is filtered by an ultrafiltration. In one embodiment the first effluent is filtered by a nanofiltration. In one embodiment a concentrate may be formed by any concentration method or device, e.g. evaporating or separating. In a preferred embodiment also organic substances are separated simultaneously.

In one embodiment of the invention the hydrolysis 11 is selected from the group of acid hydrolysis, alkaline hydrolysis, enzymatic hydrolysis and their combinations.

In one embodiment, the concentrate is treated by enzymatic hydrolysis. In one embodiment, the feeding of enzymes is phased so that the required amount of enzymes to achieve optimal hydrolysis is fed in a phased manner to the hydrolysis. In the phasing, the properties of different enzyme components are taken into account so

that preferably different enzyme mixtures are fed to the hydrolysis.

In a preferred embodiment, the enzymes as well as the enzyme mixtures formed from them are selected to hydrolysis and fermentation depending on the product fractions to be obtained. The enzyme mixtures may contain enzymes of one or more groups. Any enzymes known per se and suitable for the purpose can be used as the enzymes.

In this invention, a hydroxycarboxylic acid can include at least one hydroxycarboxylic acid or combination of different hydroxycarboxylic acids. In this connection, hydroxycarboxylic acid means any hydroxycarboxylic acid. In this connection, a hydroxycarboxylic acid product can include any hydroxycarboxylic acid or combination of different hydroxycarboxylic acids.

In one embodiment of the invention hydroxycarboxylic acid product 7 is selected from the group of glycolic acid, 3-hydroxypropanoic acid, lactic acid, succinic acid, xyloisoscacharine acid, anhydroisoscacharine acid, 3,4-dihydroxybutyric acid, 4-hydroxybutyric acid, glyceric acid, maleic acid, citric acid, oxalic acid and their combinations. Preferably, hydroxycarboxylic acid product is selected from hydroxyl carboxylic acids formed from carbohydrate materials.

In one embodiment of the invention the hydrolysis 11 and fermentation 12 are carried out at the same process stage 21. In one embodiment, in which an enzymatic hydrolysis is used in the hydrolysis step, the hydrolysis and fermentation are accomplished in one hydrolysis and fermentation process step. In one embodiment, the fermentation is continuous process. In one embodiment, batch fermentation is used.

In one embodiment the hydrolysis and fermentation unit 21 comprises a hydrolysis device 11 and

and a fermentation device 12. In one embodiment the hydrolysis device and fermentation device are separate devices.

In one embodiment, after the fermentation a suspension 5a containing the hydroxycarboxylic acid from the fermentation is concentrated 15 to form the hydroxycarboxylic acid product 7. In one embodiment the apparatus includes a second concentration device 15 for concentrating a suspension 5a containing the hydroxycarboxylic acid to form the hydroxycarboxylic acid product 7.

In one embodiment of the invention after the fermentation 12 the suspension 5a containing the hydroxycarboxylic acid is filtered 14 for separating fermentation residue 6 from the hydroxycarboxylic acid suspension 5b. In one embodiment lignin is separated by the filtering from the hydroxycarboxylic acid suspension. In one embodiment the fermentation residue is treated by an anaerobic treatment, burning and/or lignin purification.

In one embodiment, after the fermentation the suspension 5b containing the hydroxycarboxylic acid is concentrated 15 and the hydroxycarboxylic acid is separated. The concentration 15 can be made by any concentration process or apparatus known per se and suitable to be used in concentration. In a preferred embodiment, simultaneously hydroxycarboxylic acid is purified.

In one embodiment, after the fermentation the suspension containing the hydroxycarboxylic acid is concentrated by crystallization. In one embodiment after the fermentation the suspension containing the hydroxycarboxylic acid is concentrated by suspension melt crystallization. In one embodiment the suspension melt crystallization is a two-stage crystallization in which the first stage is water crystallization and the

second stage is hydroxycarboxylic acid crystallization.

The apparatus includes pH controlling means. In one embodiment pH controlling means 18a-c are arranged to control the pH during the fermentation 12 of the saccharides. In one embodiment pH controlling means 18a-c are arranged to control the pH of the first effluent 2,3 and to neutralize acidic substances of the first effluent before the hydrolysis 11 and/or fermentation 12.

In one embodiment of the invention the apparatus includes a dewaterer 10 for removing water 17 from the first effluent to provide a concentrate. In one embodiment the apparatus includes a first filtering device 15 for filtering the first effluent to provide a concentrate. The first filtering device can be any filtering device known per se and suitable for the purpose can be used in the filtering of the effluent.

In one embodiment of the invention the apparatus includes a second filtering device 14 for filtering the suspension 5a containing the hydroxycarboxylic acid after the fermentation to separate lignin and fermentation residue 6 from the hydroxycarboxylic acid suspension 5b. The second filtering device can be any filtering device known per se and suitable for the purpose can be used in the filtering of the suspension.

In one embodiment of the invention the second concentration device 15 is a suspension melt crystallization device. The second concentration device can be any concentration device known per se and suitable for the purpose can be used in the concentration of the suspension.

In hydrolysis and fermentation, any hydrolysis or fermentation process or device known per se and suitable for the purpose can be used.

In one embodiment, the concentrated hydroxycarboxylic acid product formed by fermenting is used as such. In another embodiment, the concentrated hydroxycarboxylic acid product is processed further to produce a desired product. In one embodiment of the invention the hydroxycarboxylic acid product is used as chemical, biochemical and/or polymer component.

By the method and apparatus according to the invention, it is possible to utilize different kinds of pulp mill effluents which have not been utilized cost-effectively before to form valuable products.

In the invention the second effluent is used as an adjust chemical in the pH controlling of the fermentation. The second effluent includes carbohydrates, which are simultaneously a raw stock of the hydrolysis. The use of the alkaline bleaching filtrate as the second effluent in the pH controlling gives the technical effect that the hydrogen peroxide residues in the filtrate kill all the unwanted bacteria in the first effluent.

By the invention, a good product yield is provided.

By the invention, products are provided cost-effectively and with low production costs.

EXAMPLES

In the following, the invention will be described in more detail by means of detailed exemplary embodiment with reference to the accompanying figures.

Example 1

Fig. 1 shows an apparatus for producing lactic acid which is used for producing lactic acid by the process according to the invention.

The apparatus of Fig. 1 includes an effluent feeding means 20 for feeding an effluent used as a raw

stock 2 from a pulp mill 1. The effluent feeding means
20 comprises a pipe or a duct for transporting the ef-
fluent. The effluent feeding means may also comprise
pump(s) or any other equipment needed for feeding the
5 effluent from the pulp mill to an ultrafiltration device
10. The apparatus includes an ultrafiltration device 10
for removing water 17 from the raw stock 2 and for con-
centrating the raw stock to provide a concentrate 3.
Furthermore, the process includes a hydrolysis device 11
10 based on an acid hydrolysis or alkaline hydrolysis for
hydrolyzing the concentrate 3 to form saccharides 4, and
a fermentation device 12 for fermentating the saccha-
rides 4 to form lactic acid. The apparatus includes a pH
controlling means 18 a-c for controlling and adjusting
15 the pH of the fermentation 12 by using a second efflu-
ent 16 from the pulp mill 1. Before the hydrolysis 11
the concentrate 3 can be treated in a dwell tank 13, es-
pecially if a bleaching filtrate is used as the second
effluent. The second effluent can be fed in the dwell
20 tank 13 and/or in the fermentation 12. The pH control-
ling means comprises at least one measuring device 18a
for measuring the pH in the fermentation 12 and/or be-
fore the hydrolysis 11, a feeding device 18c for feeding
the second effluent and a control unit 18b for control-
25 ling and adjusting the feeding of the second effluent on
grounds of the pH measurements. The feeding device is
pump or any other suitable equipment for feeding the se-
cond effluent from the pulp mill to the dwell tank 13
and/or the fermentation device 12. The control unit 18b
30 contains reception means to receive signals from the
measuring devices 18a, calculation means to form control
signals, and control signal transmitting means to trans-
mit the control signals formed in the control unit to
the feeding device 18c.

35 After the fermentation a suspension 5a includ-
ing lactic acid is led to a filtering device 14, where

lignin and fermentation waste 6 is filtrated from a fermentation mother liquid 5b including lactic acid. The fermentation mother liquid 5b including lactic acid is concentrated in a concentration device 15 to form concentrated lactid acid 7. The concentration device 15 is a suspension melt crystallization process where water is removed from the fermentation mother liquid 5b including lactic acid, and lactic acid 7 is separated from the fermentation mother liquid 9 for forming lactic acid 7 with concentration over 90 %. Water 8 from the concentration device 15 is led to the pulp mill 1. The fermentation mother liquid 9 is recirculated into the suspension 5a after the fermentation 12.

In this example a pulp mill bleaching filtrate is used as a raw stock. Water is removed from the raw stock to provide a concentrate with a high percentage of solids, preferably a percentage of solids of 1% to 2%. The concentrate is fed to a hydrolysis step. Preferably an acidic second effluent from the pulp mill can be added into the raw stock before the hydrolysis and/or during the fermentation.

The hydrolysis is carried out in a hydrolysis reactor at a temperature of 100 to 200°C. The duration of the hydrolysis is preferably approximately 0.5 - 2 hour. Saccharides, mainly monosaccharides, are formed in the hydrolysis.

After the hydrolysis, the saccharides are supplied to fermentation where the temperature is preferably approximately 30 - 55°C, and the duration is approximately 24 - 60 hours. In fermentation, lactic acid is formed from the saccharides. The pH of the fermentation is controlled and adjusted by using the second effluent from the pulp mill. The bacteria can be added in the fermentation, preferably after neutralization after the hydrolysis.

After fermentation, the suspension including lactic acid is filtrated for separating lignin and fermentation waste from the fermentation mother liquid including lactic acid. Separated lignin and fermentation waste can be further processed e.g. in anaerobic fermentation, by burning or in lignin purification. The fermentation mother liquid including lactic acid is concentrated by a suspension melt crystallisation for forming a concentrated lactic acid.

10

Example 2

Fig. 2 shows an apparatus for producing lactic acid which is used for producing lactic acid by the process according to the invention.

15

The apparatus of Fig. 2 includes an effluent feeding means 20 for feeding an effluent used as a raw stock 2 from a pulp mill 1. The effluent feeding means 20 comprises a pipe or a duct for transporting the effluent. The effluent feeding means may also comprise pump(s) or any other equipment needed for feeding the effluent from the pulp mill to an ultrafiltration device 10. The apparatus includes an ultrafiltration device 10 for removing water 17 from the raw stock 2 and for concentrating the raw stock to provide a concentrate 3. Furthermore, the process includes an enzymatic hydrolysis and fermentation unit 21 for hydrolyzing the concentrate 3 to form saccharides and for fermentating the saccharides to form lactic acid. In this unit 21 hydrolysis 11 and fermentation 12 are accomplished in one hydrolysis and fermentation process stage. The apparatus includes a pH controlling means 18 a-c for controlling and adjusting the pH of the fermentation 12 by using a second effluent 16 from the pulp mill 1. Before the hydrolysis 11 the concentrate 3 can be treated in a dwell tank 13, especially if a bleaching filtrate is used as the second effluent. The second effluent can be fed in

35

the dwell tank 13 and/or in the fermentation 12. The enzymes are mixed with the concentrate 3 in the hydrolysis step 11. The pH controlling means comprises at least one measuring device 18a for measuring the pH in the fermentation step 12 and/or before the hydrolysis step 11, a feeding device 18c for feeding the second effluent and a control unit 18b for controlling and adjusting the feeding of the second effluent on grounds of the pH measurements. The feeding device is pump or any other suitable equipment for feeding the second effluent from the pulp mill to the dwell tank 13 and/or the fermentation step 12. The control unit 18b contains reception means to receive signals from the measuring devices 18a, calculation means to form control signals, and control signal transmitting means to transmit the control signals formed in the control unit to the feeding device 18c.

After the fermentation a suspension 5a including lactic acid is led to a filtering device 14, where lignin and fermentation waste 6 is filtrated from a fermentation mother liquid 5b including lactic acid. The fermentation mother liquid 5b including lactic acid is concentrated in a concentration device 15 to form concentrated lactic acid 7. The concentration device 15 is a suspension melt crystallization process where water is removed from the fermentation mother liquid 5b including lactic acid, and lactic acid 7 is separated from the fermentation mother liquid 9 for forming lactic acid 7 with concentration over 90 %. Water 8 from the concentration device 15 is led to the pulp mill 1. The fermentation mother liquid 9 is recirculated into the suspension 5a after the fermentation 12.

In this example a pulp mill bleaching filtrate is used as a raw stock. Water is removed from the raw stock to provide a concentrate with a high percentage of solids, preferably a percentage of sol-

ids of 1% to 2%. The concentrate is fed to an enzymatic hydrolysis and fermentation process stage. An acidic or alkaline second effluent from the pulp mill can be added into the raw stock before the enzymatic hydrolysis step and/or during the fermentation step.

The enzymes are mixed with the concentrate by powerful mixing in a hydrolysis step at a temperature of 30 to 65°C. The duration of the hydrolysis is preferably approximately 24 hours. Saccharides, mainly monosaccharides, are formed in the hydrolysis. The saccharides are supplied to fermentation where the temperature is preferably approximately 30 - 55°C, and the duration is approximately 24 - 60 hours. In fermentation, lactic acid is formed from the saccharides. The pH of the fermentation is controlled and adjusted by using an alkaline bleaching filtrate from the pulp mill. The bacteria can be added for the fermentation.

After hydrolysis and fermentation process stage, the suspension including lactic acid is filtrated for separating lignin and fermentation waste from the fermentation mother liquid including lactic acid. Separated lignin and fermentation waste can be further processed e.g. in anaerobic fermentation, by burning or in lignin purification. The fermentation mother liquid including lactic acid is concentrated by a suspension melt crystallisation for forming a concentrated lactic acid.

The method and the apparatus according to the invention are suitable as different embodiments to be used in the manufacture of most different hydroxycarboxylic acid products.

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

CLAIMS

1. A method for manufacturing a hydroxycarboxylic acid product from lignocellulose-based raw material, characterized in that a first effluent used as a raw material is concentrated to provide a concentrate, the concentrate is treated by a hydrolysis to form saccharides, the saccharides are fermented to form hydroxycarboxylic acid, and the pH of the fermentation is controlled by using a second effluent.
2. The method according to claim 1, characterized in that the second effluent is alkaline and/or acid bleaching filtrate from the pulp mill.
3. The method according to claim 1 or 2, characterized in that the pH is controlled during the fermentation by the second effluent.
4. The method according to any one of claims 1 to 3, characterized in that the pH of the first effluent is controlled before the hydrolysis and/or fermentation by the second effluent.
5. The method according to any one of claims 1 to 4, characterized in that water is removed from the first effluent to provide a concentrate.
6. The method according to any one of claims 1 to 5, characterized in that the first effluent is filtered to provide a concentrate.
7. The method according to any one of claims 1 to 6, characterized in that the first effluent is a waste water from the pulp mill.
8. The method according to any one of claims 1 to 7, characterized in that the hydrolysis and fermentation are carried out at the same process stage.
9. The method according to any one of claims 1 to 8, characterized in that the hydrolysis is selected from the group of acid hydrolysis, alkaline

hydrolysis, enzymatic hydrolysis and their combinations.

10. The method according to any one of claims 1 to 9, characterized in that hydroxycarboxylic acid product is selected from the group of glycolic acid, 3-hydroxypropanoic acid, lactic acid, succinic acid, xyloisosaccharine acid, anhydroisosaccharine acid, 3,4-dihydroxybutyric acid, 4-hydroxybutyric acid, glyceric acid, maleic acid, citric acid, oxalic acid and their combinations.

11. The method according to any one of claims 1 to 10, characterized in that after the fermentation a suspension containing the hydroxycarboxylic acid is concentrated to form the hydroxycarboxylic acid product.

12. The method according to any one of claims 1 to 11, characterized in that after the fermentation the suspension containing the hydroxycarboxylic acid is filtered for separating fermentation residue from the hydroxycarboxylic acid suspension.

13. The method according to claim 12, characterized in that the fermentation residue is treated by an anaerobic treatment, burning and/or lignin purification.

14. The method according to any one of claims 11 to 13, characterized in that after the fermentation the suspension containing the hydroxycarboxylic acid is concentrated and the hydroxybarboxylic acid is separated.

15. The method according to any one of claims 1 to 14, characterized in that the hydroxycarboxylic acid product is used as chemical, biochemical and/or polymer component.

16. An apparatus for manufacturing a hydroxycarboxylic acid product (7) from lignocellulose-

based raw material, characterized in that the apparatus includes

- an effluent feeding means (20) for feeding a first effluent used as a raw material (2) to the apparatus;
- 5 - a first concentration device (10) for concentrating the first effluent to provide a concentrate (3);
- a hydrolysis and fermentation unit (11, 12, 21) for treating the concentrate (3) by hydrolysis to form saccharides (4) and for fermenting the saccharides (4) to
- 10 form hydroxycarboxylic acid; and
- a pH controlling means (18a-c) for controlling the pH of the fermentation (12) by using a second effluent (16).

17. The apparatus according to claim 16, characterized in that the hydrolysis and fermentation unit (21) comprises a hydrolysis device (11) and a fermentation device (12).

18. The apparatus according to claim 16 or 17, characterized in that pH controlling means (18a-c) are arranged to control the pH during the fermentation of the saccharides.

19. The apparatus according to any one of claims 16 to 18, characterized in that pH controlling means (18a-c) are arranged to control the pH of the first effluent (2) before the hydrolysis (11) and/or fermentation (12).

20. The apparatus according to any one of claims 16 to 19, characterized in that the apparatus includes a dewaterer (10) for removing water (17) from the first effluent (2) to provide a concentrate (3).

21. The apparatus according to any one of claims 16 to 20, characterized in that the apparatus includes a first filtering device (10) for filtrating the first effluent (2) to provide a concentrate (3).

22. The apparatus according to any one of claims 16 to 21, characterized in that the hydrolysis device (11) is based on hydrolysis selected from the group of acid hydrolysis, alkaline hydrolysis, enzymatic hydrolysis and their combinations.

23. The apparatus according to any one of claims 16 to 22, characterized in that the apparatus includes a second concentration device (15) for concentrating a suspension (5a) containing the hydroxycarboxylic acid to form the hydroxycarboxylic acid product (7).

24. The apparatus according to any one of claims 16 to 23, characterized in that the apparatus includes a second filtering device (14) for filtering the suspension (5a) containing the hydroxycarboxylic acid after the fermentation (12) to separate lignin and fermentation residue (6) from the hydroxycarboxylic acid suspension (5a).

25. The apparatus according to claim 23, characterized in that the second concentration device (15) is a suspension melt crystallization device.

26. The apparatus according to any one of claims 16 to 25, characterized in that the second effluent used in the pH controlling is a bleaching filtrate.

27. Use of a bleaching filtrate in controlling the pH of hydrolysis and/or fermentation of a pulp mill effluent in hydroxycarboxylic acid product manufacturing.

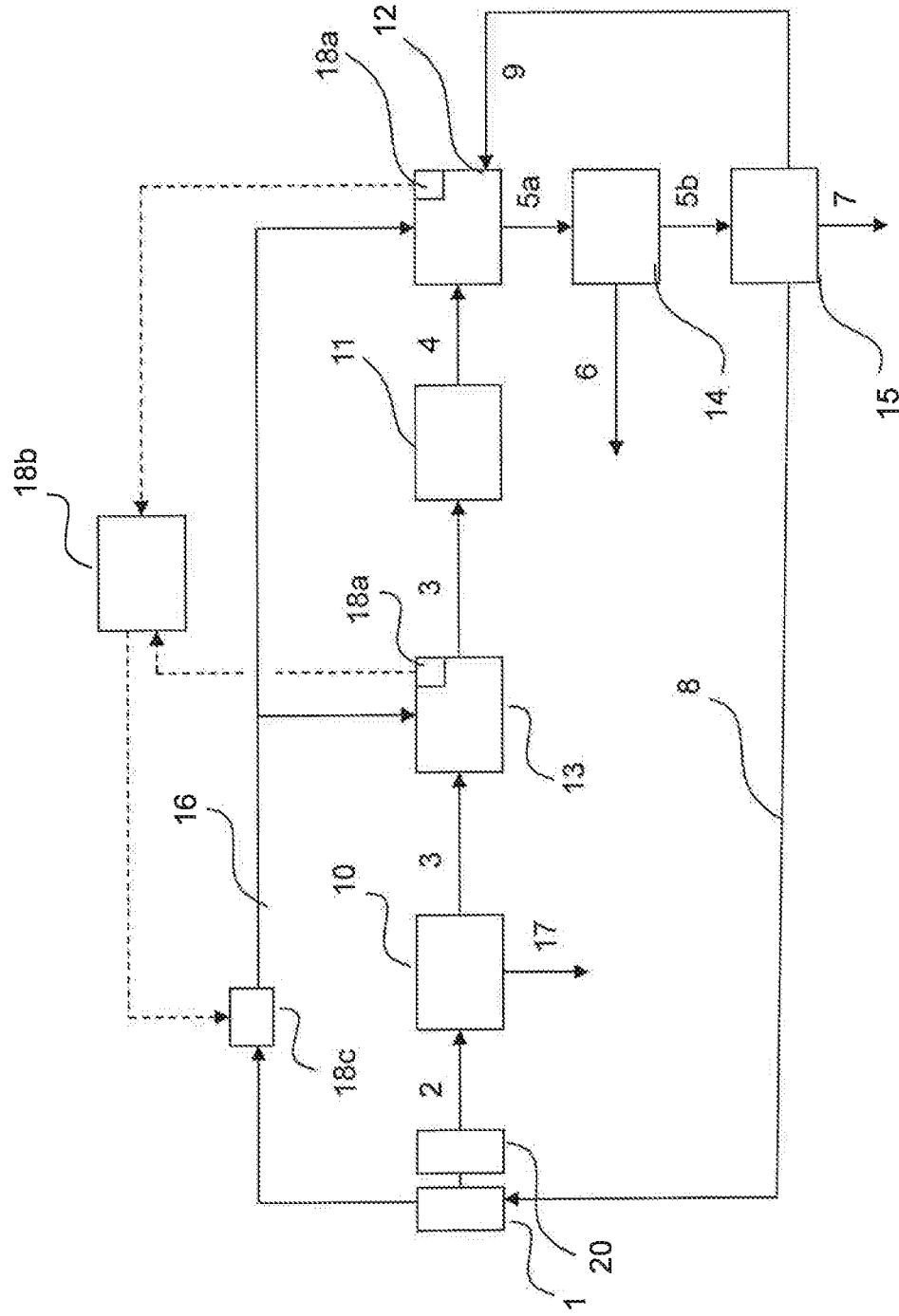


Fig. 1

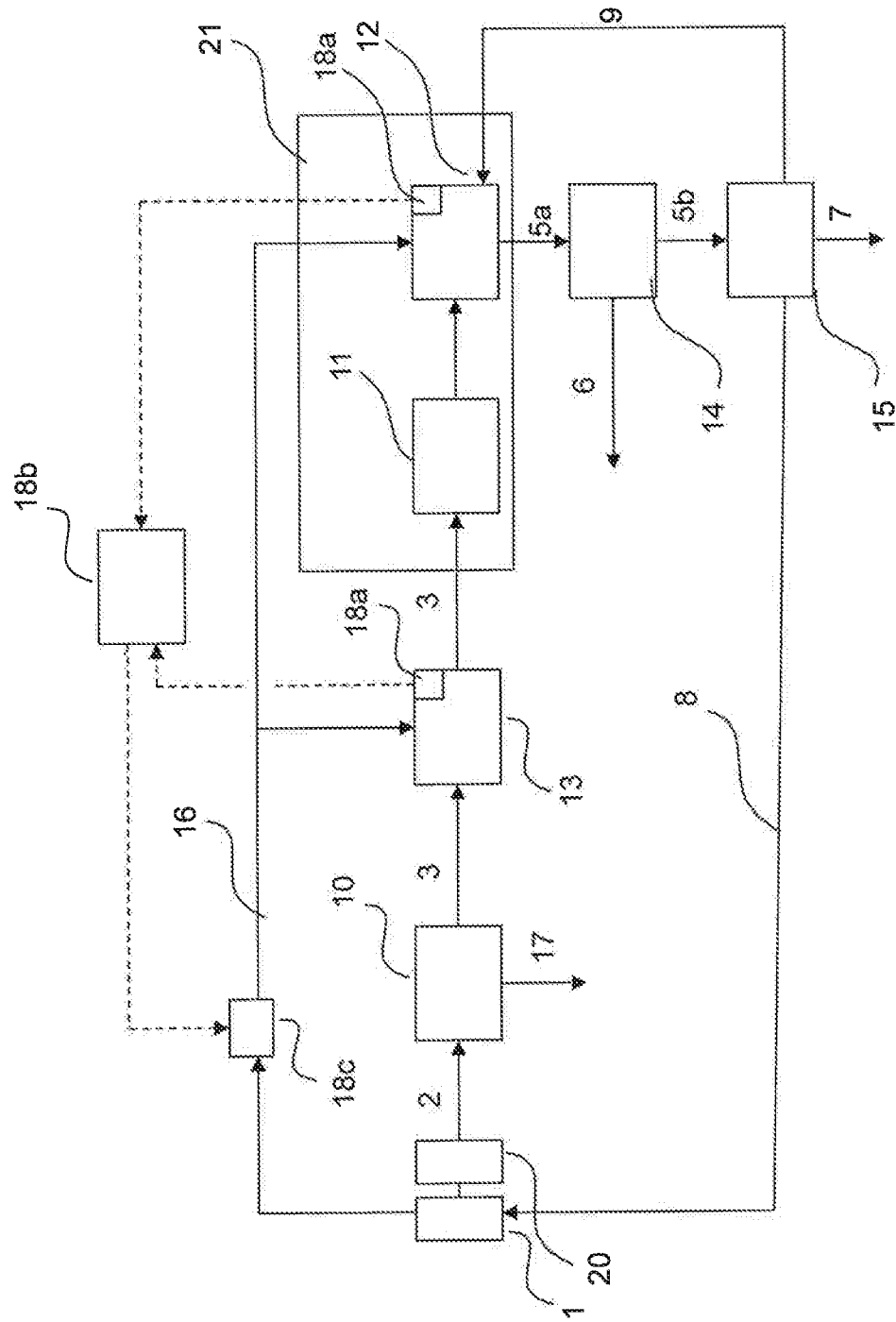


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI2012/050481

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C12P, C12M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
FI, SE, NO, DK

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI, BIOSIS, COMPENDEX, XPESP, XPESP2, CAplus, CNFULL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009025547 A1 (UNIV WAGENINGEN) 26 February 2009 (26.02.2009)	16-24, 26
Y	abstract; page 6, lines 1 and 2, page 14, line 27 – page 15, line 29, page 17, lines 5-15, page 18, line 16 – page 19, line 2, page 21, lines 6 and 7; examples 1, 7; claims 1, 16, 19; figures 1, 2A	1, 3, 5-15, 25
Y	JP 2004089177 A (INHA UNIV FOUNDATION) 25 March 2004 (25.03.2004) & abstract [online] EPOQUENET EPODOC & WPI & machine translation into English by Thomson Scientific [online] EPOQUENET TXTJPT paragraphs [0008]-[0013], [0018], [0023], [0041], [0051], [0056], [0061]-[0063], [0069]-[0072]; example 1; claims 1-3	1, 3, 5-15
A	JP 59014792 A (SANYO KOKUSAKU PULP CO) 25 January 1984 (25.01.1984) & abstract [online] EPOQUENET EPODOC & WPI	1-27



Further documents are listed in the continuation of Box C.



See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

22 October 2012 (22.10.2012)

Date of mailing of the international search report

22 October 2012 (22.10.2012)

Name and mailing address of the ISA/FI
National Board of Patents and Registration of Finland
P.O. Box 1160, FI-00101 HELSINKI, Finland

Facsimile No. +358 9 6939 5328

Authorized officer

Tomi Jukkola

Telephone No. +358 9 6939 500

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI2012/050481

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 101913747 A (UNIV SOUTH CHINA AGRICULT) 15 December 2010 (15.12.2010) & abstract [online] EPOQUENET EPODOC	1-27
A	BUDHAVARAM, NK et al. Production of lactic acid from paper sludge using acid-tolerant, thermophilic Bacillus coagulan strains. Bioresource Technology, December 2009. Vol. 100, Issue 3, pages 5966-5972 the whole document	1-27
A	WANG, LM et al. Efficient production of L-lactic acid from corncob molasses, a waste by-product in xylitol production, by a newly isolated xylose utilizing Bacillus sp. strain. Bioresource Technology, October 2010. Vol. 101, Issue 20, pages 7908-7915 the whole document	1-27
Y	WO 0056693 A1 (PURAC BIOCHEM BV et al.) 28 September 2000 (28.09.2000) abstract; page 9, lines 1-27; claim 1	25

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/FI2012/050481

Patent document cited in search report	Publication date	Patent family members(s)	Publication date
WO 2009025547 A1	26/02/2009	NZ 583521 A	28/10/2011
		US 2011177567 A1	21/07/2011
		KR 20100072212 A	30/06/2010
		JP 2010536368 A	02/12/2010
		EP 2191004 A1	02/06/2010
		EA 201070301 A1	29/10/2010
		CA 2697962 A1	26/02/2009
		AU 2008289725 A1	26/02/2009
.....			
JP 2004089177 A	25/03/2004	CN 1488759 A	14/04/2004
		KR 20040022283 A	12/03/2004
.....			
JP 59014792 A	25/01/1984	None	
.....			
CN 101913747 A	15/12/2010	None	
.....			
WO 0056693 A1	28/09/2000	JP 2011074084 A	14/04/2011
		US 6630603 B1	07/10/2003
		JP 2002540090 A	26/11/2002
		ES 2225112T T3	16/03/2005
		EP 1163200 A1	19/12/2001
		DE 60014047T T2	23/02/2006
		CN 1344241 A	10/04/2002
		BR 0009229 A	26/12/2001
		AU 3575700 A	09/10/2000
		AT 276994T T	15/10/2004
.....			

CLASSIFICATION OF SUBJECT MATTER

Int.Cl.

C12P 7/42 (2006.01)**C12P 7/48** (2006.01)**C12P 7/56** (2006.01)**C12M 1/36** (2006.01)**D21C 9/10** (2006.01)