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(71) Applicant(s)
SK Innovation Co., Ltd.

(72) Inventor(s)
KIM, Dong Hyun;KIM, Tae Wan

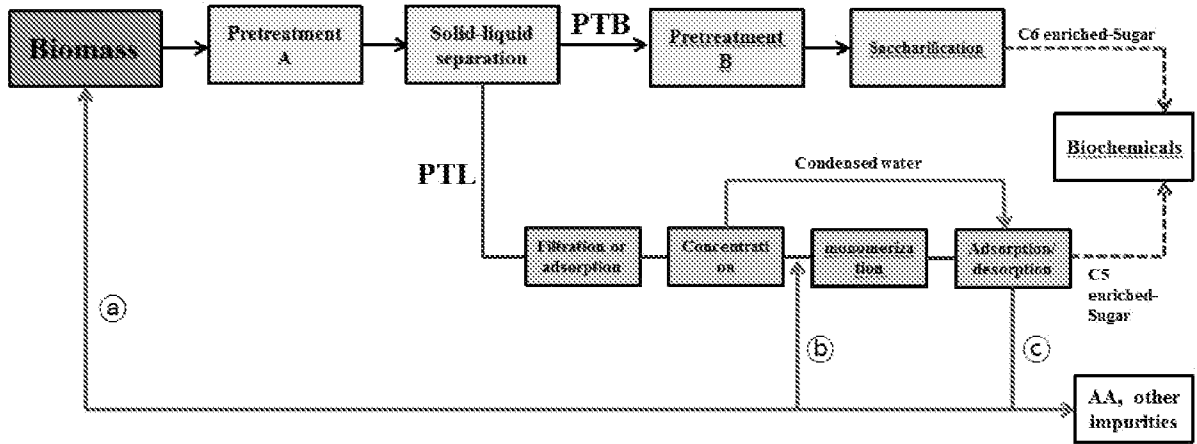
(74) Agent / Attorney
FB Rice Pty Ltd, L 23 44 Market St, Sydney, NSW, 2000, AU

(56) Related Art
US 2014/0227742 A1
US 2014/0113812 A1
Wickramasinghe et al, "Adsorptive membranes and resins for acetic acid removal from biomass hydrolysates", Desalination, 2008, Vol. 234, pp. 144-151.

ABSTRACT

The present invention relates to a method of producing saccharified solution from biomass, and more particularly to method of producing saccharified solution from biomass, in which acetic acid generated in a biomass pretreatment process is recycled so that additional supply of acid is not required, and in which corrosion of equipment by a strong acid is prevented and acetic acid that inhibits back-end saccharification and fermentation is removed in the front-end process so that the efficiency of saccharification and fermentation can be increased.

FIG. 1



METHOD OF PRODUCING SACCHARIFIED SOLUTION FROM BIOMASS**TECHNICAL FIELD**

The present invention relates to a method of
5 producing saccharified solution from biomass, and more
particularly to a method of producing saccharified
solution from biomass, which comprises recovering and
reusing acetic acid which is generated during biomass
pretreatment.

10

BACKGROUND ART

Cellulosic biomass has advantages in that it is
abundant, renewable and inexpensive, and due to such
advantages, the possibility of using the cellulosic
15 biomass as a raw material for fuel alcohol such as ethanol
or butanol is increasing. Cellulosic biomass comprises
cellulose, hemicellulose and lignin as main components,
which are strongly bonded to one another. Thus, in order
to produce a saccharified solution from the biomass in
20 high yield, these three components need to be separated
from one another by pretreatment.

Among the three components, cellulose has the
properties of being thermally stable and being soluble in
acid, and hemicellulose has the properties of being
25 thermally unstable and being soluble in acid. On the
other hand, lignin has the properties of being thermally
stable and being soluble in alkali.

In order to efficiently separate these components from one another, which have different properties as described above, various pretreatment processes have been developed. Among processes that have been developed, the most ideal pretreatment method is to selectively remove the lignin component without loss of the cellulose component to thereby convert the cellulosic raw material into a form that is easy to enzymatically saccharify.

Major pretreatment methods include mechanical crushing, alkali swelling, dilute acid hydrolysis, hydrothermal pretreatment and steam explosion pretreatment methods, and combinations of such methods may also be used.

Among these methods, the hydrothermal pretreatment method can separate hemicellulose as a liquid by water under mild conditions while allowing cellulose and lignin to remain as a solid. It is a method that increases the recovery of hemicellulose having low thermal stability by the use of mild conditions.

Furthermore, in the steam explosion pretreatment method, a raw material is charged into a pressurized reactor and saturated steam is blown into the reactor to cause a pressurized reaction, and then pressure is suddenly discharged from the reactor, whereby an exploded raw material can be obtained. In this procedure, hydrolysis of hemicellulose may occur, or the structure of lignin may also be broken. This method has high energy

efficiency, because the raw material does not need to be finely crushed.

In selection of an efficient pretreatment one from various pretreatment methods, a reduction in investment in application of an actual commercial process needs to be considered together with an increase in sugar yield. In the case of an acid treatment method, pretreatment efficiency can be increased by increasing pretreatment severity, but commercialization of the process can be difficult due to problems associated with equipment corrosion. In addition, when acid is continuously used, the production cost can be increased due to an increase in operating expenditure (OPEX).

US Patent Publication No. 2014-0154759 discloses a process for producing low-ash biomass for combustion or pellets. The disclosed process comprises treating biomass with acetic acid, separating the treated biomass into a liquid portion and a solid portion, extracting low-ash biomass from the solid portion, and removing acetic acid from the liquid portion by evaporation, thereby producing saccharified solution. However, it has disadvantages in that, because acetic acid is removed by evaporation, a large amount of cost is required for separation of acetic acid, and because the solid portion is used for production of a fuel for combustion, the efficiency of production of the saccharified solution is deteriorated.

US Patent Publication No. 2015-0051385 discloses a method for liquid/liquid separation of lignocellulosic biomass to produce saccharified solution. The disclosed method comprises pretreating biomass with heated acetic acid, separating the pretreated biomass into a lignin-containing liquid portion and a cellulose-containing solid portion, and recycling acetic acid from the liquid portion. However, it has disadvantages in that, because heated acetic acid is used, much cost is required to maintain high temperature, and because distillation is used to separate acetic acid, the overall operating cost is high.

Accordingly, the present inventors have made extensive efforts to solve the above-described problems, and as a result, have found that, a xylo-oligomer-containing fraction and a fraction containing cellulose and lignin, which are produced from biomass, are separated from each other and saccharified, after which acetic acid in the xylo-oligomer-containing fraction is separated by concentration and adsorption and recycled to a process for pretreatment of biomass and a portion of the recycled acetic acid is introduced into the saccharification process, so that the efficiency of the pretreatment can be increased without supply of acid, corrosion of equipment by a strong acid can be prevented, and the efficiency of saccharification can be increased by performing the saccharification process after separation of acetic acid

which inhibits a back-end saccharification or fermentation reaction, thereby completing the present invention.

SUMMARY OF INVENTION

The present invention relates to a method in which acetic acid produced in biomass pretreatment/saccharification processes is recycled to thereby reduce the operating cost and which increases the efficiency with which saccharified solution is produced from biomass.

DETAILED DESCRIPTION OF THE INVENTION

In one aspect there is provided a method of preparing saccharified solution from biomass, comprising: (a) firstly pretreating biomass and separating a pretreated biomass into a xylo-oligomer-containing fraction and a fraction containing cellulose and lignin; (b) secondly pretreating the fraction containing cellulose and lignin and then saccharifying by using enzyme, thereby obtaining C6-enriched sugar; and (c) filtering the xylo-oligomer-containing fraction and removing substances that inhibit monomerization and fermentation by an adsorbent resin, and then removing a considerable amount of water by concentration process, and then monomerizing a concentrated fraction, thereby obtaining C5-enriched sugar, wherein the C5-enriched sugar is obtained by adsorption and desorption of acetic acid

from the monomerized liquid in the step (c), and wherein acetic acid produced in a first pretreatment and/or monomerization in the step (c) is recovered in the desorption and recycled to the first pretreatment.

5

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow chart showing a method of producing saccharified solution from biomass according to an embodiment of the present invention.

10 Explanation on Symbols

Ⓐ: acetic acid recycled to the biomass pretreatment process

Ⓑ: a portion of the recycled acetic acid introduced into the saccharification process

15 Ⓒ: acetic acid, furfural and HMF discharged to the outside

BEST MODE FOR CARRYING OUT THE INVENTION

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention pertains. Generally, the nomenclature used herein and the experiment methods, which will be described below, are those well known and commonly employed in the art.

In an example of the present invention, biomass was pretreated, and then a xylo-oligomer-containing fraction

and a fraction containing cellulose and lignin were separated from each other and subjected to a saccharification reaction. The xylo-oligomer-containing fraction was filtered and passed through an adsorbent resin to remove fermentation-inhibiting substances such as fine powder and inorganic substances, after which it was concentrated to remove a considerable amount of water and saccharified through a monomerization process. After monomerization, the saccharified liquid was subjected to adsorption and desorption processes to separate acetic acid which was then recycled to the biomass pretreatment process. As a result, it was found that high saccharification efficiency was achieved without additional supply of acid and that the saccharification efficiency was increased as a result of performing the saccharification process after separation of acetic acid which inhibits a back-end saccharification or fermentation process.

Therefore, the present invention is directed to a method of preparing saccharified solution from biomass, comprising: (a) firstly pretreating biomass and separating a pretreated biomass into a xylo-oligomer-containing fraction and a fraction containing cellulose and lignin; (b) secondly pretreating the fraction containing cellulose and lignin and then saccharifying by using enzyme, thereby obtaining C6-enriched sugar; and (c) filtering the xylo-oligomer-containing fraction and removing substances that

inhibit monomerization and fermentation by an adsorbent resin, and then removing a considerable amount of water by concentration process, and then monomerizing a concentrated fraction, thereby obtaining C5-enriched sugar, wherein the C5-enriched sugar is obtained by adsorption and desorption of acetic acid from the monomerized liquid in the step (c), and wherein acetic acid produced in a first pretreatment and/or monomerization in the step (c) is recovered in the desorption and recycled to the first pretreatment.

FIG. 1 is an overall schematic view showing a process of producing saccharified solution from biomass according to the present invention.

1. Process for pretreatment and solid-liquid separation of biomass (step (a))

In the first step of the method for producing saccharified solution according to the present invention, biomass is first pretreated (pretreatment A in FIG. 1) and is solid-liquid separated into a xylo-oligomer-containing fraction (pretreated fraction (PTL)) and a fraction (pretreated biomass (PTB)) containing cellulose and lignin.

2. Saccharification process

2-1. Process for saccharification of PTB (step (b))

In the first step of the saccharification process in the method for producing saccharified solution according to the present invention, the fraction (PTB) containing

cellulose and lignin, separated in step (a), may be pretreated (pretreatment B in FIG. 1), and then enzymatically saccharified to obtain C6 enriched-sugar.

5 2-2. Process for saccharification of PTL (step (c))

In the second step of the saccharification process in the method for producing saccharified solution according to the present invention, the xylo-oligomer-containing fraction (PTL), separated in step (a), may be
10 filtered and passed through an adsorbent resin to remove fine powder and fermentation-inhibiting substances such as cations, HMF, furfural, etc., and it may be concentrated to remove a considerable amount of water, and then saccharified by a physical/chemical method. Then, the
15 saccharified material may be subjected to an adsorption/desorption process for AA recovery, thereby obtaining high-purity C5-enriched sugar.

Herein, the considerable amount of water corresponds to 40-50 vol% of the total volume of water. The amount of
20 water removed may preferably be 10-80 vol%, more preferably 40-50 vol%.

Because the PTL contains a large amounts of microbial fermentation-inhibiting components (mainly acetic acid, HMF, and furfural), concentration and
25 adsorption processes for removing these components are required.

Acetic acid (low-concentration acetic acid obtained by concentration and high-concentration acetic acid separated by adsorption) recovered in these processes may be introduced into the pretreatment process to thereby
5 increase pretreatment efficiency.

The present invention may use a portion of acetic acid derived from biomass that continues to be produced in the pretreatment process, but not strong acid such as sulfuric acid, hydrochloric acid, phosphoric acid or the
10 like that has been widely used in an existing pretreatment process. The pretreatment process that is used in the present invention is an economical and efficient pretreatment process in which the severity of hydrothermal treatment (a function of temperature, time and pH) is
15 increased while acetic acid is produced from the acetyl group of hemicelluloses that is a component of partially recycled biomass, thereby increasing the pretreatment effect.

The method for producing saccharified solution
20 according to the present invention may further comprise a step of supplying condensed water, separated in the concentration process in step (c), to the desorption process so that the supplied condensed water is used as water for desorption in the processes for adsorption and
25 desorption of acetic acid.

As shown in FIG. 1, when the concentration process is carried out after filtration and the adsorption process

for removal of impurities in step (c), there are advantages in that the amount of heat required for heating in the monomerization process can be reduced and the throughput of the monomerization process can be reduced, 5 thereby reducing capital expenditure (CAPEX). Furthermore, condensed water generated in the concentration process can be supplied to the desorption process, and may be used for desorption after heating, but is not limited thereto. Herein, the concentration of acetic acid separated in the 10 desorption process is preferably 5-30 w%.

In the concentration process, acetic acid is separated by evaporation with water. For this reason, acetic acid that is separated in the concentration process is diluted in water, and thus is present at a relatively 15 low concentration. In the desorption process, acetic acid and impurities are adsorbed and discharged independently of water, and thus a relatively high concentration of acetic acid is separated.

In the present invention, a portion of the acetic acid recycled may be introduced into the monomerization 20 process of step (c). In the PTL treatment process, the oligomer is converted to C5-enriched sugar by monomerization. When acid is supplied to the monomerization process, the rate of conversion to C5- 25 enriched sugar will increase. Thus, as shown in FIG. 1, a portion of acetic acid recovered from the desorption process may be introduced into the monomerization process

to thereby increase the conversion rate of the monomerization reaction. Although the amount of acetic acid recovered and reused varies depending on the acetyl content of biomass, the amount of acetic acid generated is 5 0.17-1.67 ton/hr when biomass is treated in an amount of 49 dry ton/day. The ratio of the amount of acetic acid recycled to the pretreatment process (Ⓐ in FIG. 1) to the amount of acetic acid discharged to the outside (Ⓒ in FIG. 1) is 90:10-98:2, which corresponds to a concentration of 10 5-30%. When low-concentration acetic acid (AA) is applied, severity can be increased by controlling reaction temperature and reaction time, thereby suppressing the production of inhibitors at low pH, and when high-concentration acetic acid (AA) is applied, severity can be 15 reduced by controlling reaction temperature and reaction time, thereby reducing the amount of steam used and increasing productivity. This makes efficient production possible. A portion of the recovered acetic acid (AA) may be introduced into the front end of the PTL monomerization 20 process ("b" in FIG. 1) to thereby increase the efficiency of monomerization of the PTL. Herein, the weight of the AA that is introduced is preferably adjusted such that the acetic acid (AA) concentration of the front-end stream of the PTL monomerization process is 30-50%.

25 Moreover, the acetic acid recovered may be completely recycled to the pretreatment process, and if the concentration of acetic acid in the production system

of the present invention increases to cause side reactions, a portion or all of the acetic acid may be discharged to the outside. However, the total amount of acetic acid which is recycled to the pretreatment A process, acetic acid which is introduced into the monomerization process, and acetic acid which is discharged to the outside, should be the same as the amount of acetic acid which is recovered from the acetic acid (AA) adsorption process, in order to prevent the accumulation of acetic acid in the production system to thereby minimize side reactions.

In the present invention, the concentration in step (c) may be vacuum concentration. The concentration process is a process of evaporating an object using heat. Thus, as the boiling point of the object is lower, concentration may be achieved using a smaller amount of heat, and for this reason, the boiling point of the object is preferably lowered. Accordingly, the concentration process is preferably performed in a vacuum so that the amount of heat consumed can be minimized. More preferably, the concentration process may be performed at a pressure of 10-300 Torr.

In the present invention, the adsorption of step (c) may use activated carbon as an adsorbent. As the adsorbent used in the adsorption process of the present invention, any adsorbents can be used without any limitation as long as they adsorb acetic acid, but activated carbon, zeolite, silica gel, aluminum sulfate or

an ion exchange resin such as a cation exchange resin is preferably used which is stable under acid conditions and does not react with water.

5

EXAMPLES

Hereinafter, the present invention will be described in further detail with reference to examples. It will be obvious to a person having ordinary skill in the art that these examples are illustrative purposes only and are not
10 to be construed to limit the scope of the present invention.

Example 1: Production of Saccharified Solution from Biomass through Recycling of Acetic Acid

15 As shown in FIG. 1, biomass was first hydrothermally pretreated at a temperature of 185°C for 5 minutes, and then separated into a fraction containing cellulose and lignin and a xylo-oligomer-containing fraction. The fraction containing cellulose and lignin was treated
20 mechanically, pretreated, and then saccharified to produce C6-entiched sugar. The xylo-oligomer-containing fraction was filtered and passed through an adsorbent resin to remove fine powder and cations, which inhibits the corresponding process, after which it was concentrated to
25 remove a considerable amount of water and subjected to a monomerization process. After the monomerization process, the resulting material was subjected to adsorption and

desorption processes using activated carbon to separate and recover acetic acid (AA). Herein, condensed water obtained in the concentration process was used as water for desorption. Furfural and HMF were separated and removed from impurities separated by the desorption process, and the remaining high-concentration (70 wt%) acetic acid was recovered and recycled to the first pretreatment process. A portion of the acetic acid recycled was introduced into the monomerization process.

Although the amount of acetic acid recovered and reused varies depending on the acetyl content of biomass, the amount of acetic acid generated is 0.276 ton/hr when biomass is treated in an amount of 49 dry ton/day. The ratio of the amount of acetic acid recycled ($\text{a}+\text{b}$) to the amount of acetic acid discharged to the outside (c) among the acetic acid adsorbed in the adsorption process is 90:10-98:2, which corresponds to a concentration of 5-30%. When low-concentration acetic acid (AA) was applied, severity can be increased by controlling reaction temperature and reaction time, thereby suppressing the production of inhibitors at low pH, and when high-concentration acetic acid (AA) is applied, severity can be reduced by controlling reaction temperature and reaction time, thereby reducing the amount of steam used and increasing productivity. This made efficient production possible. A portion of the recovered acetic acid (AA) was introduced into the front end of the PTL monomerization

process in order to increase the efficiency of monomerization of the PTL. Specifically, the weight of recovered acetic acid (AA) into the front end of PTL monomerization process was controlled such that the acetic acid (AA) concentration of the front-end stream of the PTL monomerization process would be 30-50 wt%.

According to the Example of the present invention, acetic acid generated in the pretreatment process was recovered and concentrated, and the concentrated acetic acid was introduced into the pretreatment process to increase the severity of the process, thereby increasing the pretreatment effect. According to the present invention, because acetic acid generated in the pretreatment process is used, a separate chemical cost is not incurred, and thus the operating expenditure does not increase, and because a weak acid, not a strong acid, is used, equipment corrosion does not occur, and thus investment in plant construction decreases. In addition, because acetic acid that acts as an inhibitor in back-end saccharification and fermentation processes is removed in the front-end process, the efficiency of saccharification and fermentation can be increased. Furthermore, in the process of recovering acetic acid, other impurities such as furfural and HMF, etc., which are high-value-added compounds, can also be recovered.

INDUSTRIAL APPLICABILITY

In the method of producing saccharified solution from biomass according to the present invention, acetic acid is recycled, and thus additional supply of acid is not
5 required in pretreatment of biomass and monomerization of pretreated liquid. Furthermore, saccharification and fermentation processes are performed after separation of acetic acid that inhibits a back-end saccharification or fermentation reaction, and thus saccharification
10 efficiency and fermentation efficiency increase. Accordingly, the present invention is useful for efficient production of saccharified solution.

Although the present invention has been described in
15 detail with reference to the specific features, it will be apparent to those skilled in the art that this description is only for a preferred embodiment and does not limit the scope of the present invention. Thus, the substantial scope of the present invention will be defined by the
20 appended claims and equivalents thereof.

What is claimed is:

1. A method of preparing saccharified solution from biomass, comprising:

(a) firstly pretreating biomass and separating a pretreated biomass into a xylo-oligomer-containing fraction and a fraction containing cellulose and lignin;

(b) secondly pretreating the fraction containing cellulose and lignin and then saccharifying by using enzyme, thereby obtaining C6-enriched sugar; and

(c) filtering the xylo-oligomer-containing fraction and removing substances that inhibit monomerization and fermentation by an adsorbent resin, and then removing a considerable amount of water by concentration process, and then monomerizing a concentrated fraction, thereby obtaining C5-enriched sugar,

wherein the C5-enriched sugar is obtained by adsorption and desorption of acetic acid from the monomerized liquid in the step (c), and

wherein acetic acid produced in the step (a) or (c) is recovered in the desorption and recycled to the step (a).

2. The method of claim 1, further comprising supplying condensed water produced in the concentration process in the step (c), to the desorption so as to use as water for desorption in adsorption and desorption of acetic acid.

3. The method of claim 1, wherein a concentration of acetic acid separated in the desorption is 5-30 w%.

4. The method of claim 1, wherein a portion of recycled acetic acid is introduced into the monomerization of the step (c).

5. The method of claim 4, wherein a ratio of an amount of recycled acetic acid to a first pretreatment to an amount of discharged acetic acid is 90:10-98:2, and acetic acid is introduced so as to be 30-50% of the acetic acid concentration of a front-end stream of the monomerization.

6. The method of claim 1, wherein the concentration process in the step (c) is vacuum concentration.

7. The method of claim 6, wherein the vacuum concentration is performed at a pressure of 10-300 Torr.

8. The method of claim 1, wherein the adsorption of the step (c) uses the adsorbent resin selected from the group consisting of activated carbon, zeolite, silica gel, aluminum sulfate and a cation exchange resin.

FIG. 1

