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(54) Title: SYSTEM AND METHOD FOR INCREASING CARBOHYDRATE AND LIGNIN CONCENTRATION IN HYDRO-LYSATE OF BIOMASS PRETREATMENT

(57) Abstract: A system and method are disclosed for pretreating biomass. Countercurrent flowthrough and recycled hydrolysate are employed to pretreat the biomass. The concentrations of carbohydrate and lignin in the final hydrolysate are increased. Temperature ingredients in the pretreatment vessel may be used to increase the pretreatment efficiency. By recycling the heat and the liquid, the disclosed methods help reduce energy and/or water used in the processes.

SYSTEM AND METHOD FOR INCREASING CARBOHYDRATE AND LIGNIN CONCENTRATION IN HYDROLYSATE OF BIOMASS PRETREATMENT

RELATED APPLICATIONS

[0001] This application claims priority of U. S. Provisional Application No. 61/570,635 filed on December 14, 2011, the content of which is hereby incorporated into this application by reference.

I. Field of the Invention

[0002] This disclosure pertains to treatment of biomass to enhance conversion efficiency from biomass to biofuels, or other useful chemicals. More specifically, the disclosure relates to a method for increasing the hydrolysate concentration in a flowthrough pretreatment system.

II. Background

[0003] Cellulosic biomass is useful for generating biofuels such as ethanol and other valuable chemicals. Many cellulosic biomass such materials specifically known as lignocellulosic materials, or biomass, (e.g. wood and solid wastes), have been used as source material to generate carbohydrates, which in turn may be used to produce ethanol, as well as other products. However, large-scale utilization of plant biomass is hindered, at least in part, by the lack of technologies capable of efficiently converting the biomass into component fractions or reactive intermediates at a low cost. For example, most plant biomass is resistant to the digestion by cellulase, which may lead to low cellulose hydrolysis yields.

[0004] Pretreatment of biomass may render the biomass more amenable to enzymatic digestion. For instance, biomass components (e.g., lignin) that impede access to cellulase enzymes may be removed during pretreatment. Pretreatment may also cause structural changes (e.g. particle size, porosity, surface area) to the biomass which may render them more accessible to enzymes. Various biomass pretreatment technologies have been developed. Examples of these developments include use of dilute acids or bases, steam explosion, autohydrolyisis, controlled pH, AFEX, and aqueous ammonia pretreatment.

[0005] Autohydrolysis pretreatment employs hot water or steam to pretreat biomass. However, high pretreatment severity (e.g. temperature >190°C) is generally required to produce digestible substrate which may result in high losses of hemicellulose sugars. For instance, depending on residence time, xylose losses can be as high as 25%, or even higher. In addition, inhibitors released from the biomass and produced in the course of sugar and lignin degradation may negatively affect the qualities of the insoluble materials, such as substrate fermentability and digestibility.

[0006] In conventional steam pretreatment in which the residence time of the solids and liquid is the same, whether operated in batch or continuous mode, dissolved biomass components may degrade once they are dissolved or suspended in solution. In addition, solubilized lignin and hemicellulose components may precipitate during cooling, which decreases the reactivity of the biomass to enzymatic hydrolysis.

[0007] One approach for improving pretreatment effectiveness involves washing of the solid biomass after closed-system pretreatment ("post-washing"). Post-washing at high temperatures, for example, at 140°C, helps produce reactive biomass material and also removes some lignin and hemicellulose solubilzation products. The amount of lignin and hemicellulose solubilzation products removed in post- washing may not be as much as the amount that would be removed if washing were done at pretreatment reaction temperatures. Furthermore, once-through washing typically dilutes solubilized components, making them more expensive to recover or process in subsequent steps. Although post-washing of solid biomass at moderate temperatures (e.g., 100°C) and under atmospheric pressure may help eliminate certain complexities, it is not very efficient in producing adequate yield of the biomass solids and makes achieving sterilization more difficult.

[0008] Another approach for enhancing pretreatment effectiveness involves flowing hot water, or acid, through the solid biomass, also known as flowthrough pretreatment. Flowthrough pretreatment with hot water, or very dilute acid, may effectively remove hemicellulose and lignin, and may generate highly active substrate (Liu & Wyman, 2003, 2004). For example, hot water flowthrough pretreatment removes significant amount of dissolved hemicellulose and lignin thus avoiding precipitation. When flowthrough pretreatment is carried out with hot liquid at a temperature of, for example, between 120°C and 240°C, the reactivity of the

resulting biomass solids are several-fold greater than that of a closed-system control. However, conventional flowthrough operation uses too much energy and water. Moreover, the hemicellulose hydrolyzate recovered from flowthrough pretreatment may be too dilute which increases the cost of subsequent sugar recovery.

SUMMARY

[0009] The presently disclosed instrumentalities advance the art by providing systems and methods for obtaining hydrolysate from biomass. More particularly, the disclosed methodology may result in increased concentration of carbohydrate and/or lignin in the hydrolysate obtained from flowthrough pretreatment of biomass. By recycling the hydrolysate in the flowthrough, the disclosed methods also reduce the consumption of water and energy.

[0010] Flowthrough pretreatment of biomass has been reported as being infeasible because the process uses excessive amount of energy and water. In one embodiment, the disclosed process uses counter-current flowthrough in which the direction of the pretreatment liquid is opposite to the flow of the biomass in the vessel. As compared to batch pretreatment or co-current flowthrough, counter-current flowthrough may substantially reduce the amount of energy and water required for the process.

[0011] In addition, the disclosed process may also help reduce carbohydrate degradation and increase carbohydrate concentration in the hydrolysate obtained from pretreatment of the biomass. When the substantially dry biomass is mixed with hydrolysate rather than water, the water in the hydrolysate may act as a solvent to dissolve the carbohydrate and lignin, thus preventing dilution of the hydrolysate. In another aspect, because the incoming hydrolysate may enter the vessel and is washed out directly with minimum exposure to reaction conditions, degradation of the carbohydrate may be kept to the minimum.

[0012] In one embodiment, the disclosed system may include a vessel in which the biomass may make contact with the pretreatment liquid. The vessel may have a solid inlet, a solid outlet, a liquid inlet and a liquid outlet. The biomass may enter the vessel through the solid inlet and may flow in the vessel from the solid inlet towards the solid outlet. In one aspect, the vessel may be oriented such that the flow

of the biomass in the vessel is driven by gravity. In another aspect, the flow rate of the biomass may be regulated.

[0013] In one embodiment, liquid (also referred to as a "pretreatment liquid"), such as water or other liquid, may be passed through the biomass to generate a flowthrough mixture (also referred to as an "effluent" or "reactor effluent"). The pretreatment liquid may be heated to a temperature that is higher than room temperature before entering the vessel. The effluent may contain the liquid and one or more components of the biomass. The pretreatment liquid may flow from the liquid inlet towards the liquid outlet. In one aspect, the liquid may flow in a direction that is opposite to the flow of the biomass. In another aspect, the liquid may flow in the same direction as the flow of the biomass. The flow rate of the pretreatment liquid may be regulated. In one embodiment, the flow rate of the pretreatment liquid inside the vessel is at least 2 times, or 2-10 times faster than the mass flow rate of the biomass. In another embodiment, the flow rate of the pretreatment liquid inside the vessel is 3-4 times faster than that of the biomass inside the vessel.

[0014] As the pretreatment liquid makes contact with the biomass, various component of the biomass, such as carbohydrate, lignin, may enter the pretreatment liquid forming a hydrolysate. The hydrolysate may exit the vessel through the liquid outlet. In one aspect, the exiting hydrolysate may be subject to a fermentation process. In another aspect, the system may contain a means, such as a conduit, for conveying the hydrolysate from the liquid outlet back into the vessel, where the recycled hydrolysate makes further contact with the biomass. The conduit may be an integral part of the vessel. Alternatively, the conduit may be connected to but separate from the vessel.

[0015] In another embodiment, the pretreatment liquid may be fresh water, dilute acid base or salt solution, or recycled hydrolysate. In one aspect, the pretreatment liquid and the biomass may enter the vessel separately. In another aspect, the pretreatment liquid may be pre-mixed with the biomass outside of the vessel. The liquid and the biomass may then enter the vessel in the form of a pre-mix.

[0016] In another embodiment, the system may contain a first heating means in the conduit which may heat the hydrolysate as it flows through the conduit. In another embodiment, the system may also contain a second heating means. In one aspect, the second heating means may be located inside the vessel. In another aspect,

the second heating means may help generate a temperature gradient in the vessel, with the temperature increasing from the solid inlet to the solid outlet. The temperature gradient may be in the range of from 20°C to 240°C. In another aspect, the temperature gradient may be in the range of from 50°C to 220°C, 130°C to 220°C, or 150°C to 220°C, with temperature increasing from the side of the solid inlet. In one embodiment, when the flowthrough pretreatment is a counter-current system, the hydrolysate (liquid) outlet is on the same side of the vessel as the solid (biomass) inlet.

[0017] In one embodiment, a certain amount of the biomass may be mixed in the vessel with a first inflow of a liquid. In another embodiment, the biomass may be mixed with a liquid before entering the vessel and may enter the vessel with the liquid as a pre-mix. As the biomass moves (or flows) through the vessel, the biomass makes contact with the liquid and various components (e.g., carbohydrate, lignin, etc.) are dissolved in the liquid forming a hydrolysate. In another embodiment, the flow of the pretreatment liquid may be in a direction opposite to the flow of the biomass in the vessel.

[0018] After making contact with the biomass, the liquid may exit through the liquid (hydrolysate) outlet of the vessel as a first effluent. The first effluent may contain carbohydrate, lignin, among others, forming a hydrolysate of the biomass. In one aspect, the first effluent may be subject to a fermentation process. In another aspect, the first effluent may pass through a conduit and enter the vessel as a second inflow. The second inflow may be mixed with the solid biomass outside of the vessel forming a pre-mix. The pre-mix may then enter the vessel through the solid inlet.

[0019] The biomass may exit the vessel through the solid outlet. Because the exiting biomass may take away certain amount of liquid from the vessel, additional fresh liquid may be included in the second inflow. Thus, in one embodiment of the instant disclosure, the second inflow may include the first effluent and the additional fresh liquid. This process may be repeated 5-100 times. In one aspect, the process may be repeated at least 10 times. In another aspect, in a continuous operation, the process may be repeated indefinitely unless the operation is shut down for maintenance or other reasons.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] Figure 1 is a schematic drawing of an exemplary flowthrough pretreatment system showing major components of the system.

[0021] Figure 2 illustrates the calculation of hydrolysate concentration in systems using hydrolysate for flowthrough pretreatment and in systems using water for flowthrough pretreatment.

[0022] Figure 3 shows the oligomer concentration, xylan hydrolysis conversion, and the concentration of degradation product in a counter-current flowthrough system with five scenarios of temperature gradients.

[0023] Figure 4 shows the oligomer concentration, xylan hydrolysis conversion, and the concentration of degradation product in a co-current flowthrough system with five scenarios of temperature gradients.

[0024] Figure 5 compares the concentrations of degradation product [P] in (1) co-current, (2) counter-current and (3) counter-current with temperature gradient flowthrough systems.

DETAILED DESCRIPTION

[0025] The present disclosure provides systems and methods for increasing the recovery of carbohydrate, lignin, proteins, and other useful materials from biomass. The methods may also be used to increase the concentration of these materials recovered from biomass.

[0026] In one embodiment, a vessel is used for flowthrough pretreatment of the biomass. As shown in Fig. 1, biomass (stream 102) may enter the vessel (or reactor) through a solid inlet. The biomass may be any materials that contain molecules that can be broken down to fermentable sugars. In one embodiment, the biomass is a lignocellulosic biomass. Typically, the solid biomass that enters the vessel is dry or mostly dry and is mixed with a pretreatment liquid in the vessel. The pretreatment liquid may be water, an acid or base solution, a salt solution or a hydrolysate of the biomass.

[0027] Biomass may enter the vessel through the solid inlet. In one embodiment, the biomass may be pre-mixed with a liquid before entering the vessel. By way of example, the solid biomass (stream 102) may be mixed with the recycled hydrolysate (stream 106) to form a stream 110, which is then fed into the vessel (Fig.

1). The biomass may move (or flow) in the vessel and exit the vessel from a solid outlet (stream 122).

[0028] The pretreatment liquid may enter the vessel through a liquid inlet as stream 126 (Fig. 1). In one embodiment, the liquid may flow in a direction opposite from the direction of the biomass movement. In another embodiment, the liquid may flow in the same direction as that of the biomass movement.

[0029] The pretreatment liquid may exit the vessel as a hydrolysate (stream 114 in Fig. 1) through a liquid outlet. In one aspect, the hydrolysate of stream 114 may be divided into two separate portions: one portion (stream 106) may be returned to the vessel to pretreat more biomass; the other portion (stream 118) may be subject to further processing as a hydrolysate. Stream 106 may be mixed with incoming biomass to help remove air from the biomass. Stream 118 may contain significant amount of carbohydrate and lignin and may be subject to further separation or fermentation processes.

[0030] The process of using recycled hydrolysate to pretreat the biomass as described above may be repeated for many cycles. The disclosed process may be applied to single stage or multi-stage reactors. Additional inlets and outlets may exist between the two ends of a vessel for multi-stage reactors or for a single-stage reactor having multiple reaction zones. In one aspect, the vessel or reactor may have uniform temperature. In another aspect, the vessel or reactor system may have a temperature gradient. For example, the temperature may increase from the end of solid inlet towards the solid outlet.

[0031] In one aspect, the liquid inlet and the solid outlet may have separate openings on the vessel, or the liquid outlet and the solid inlet may have separate openings on the vessel. In another aspect, the liquid inlet and the solid outlet may share the same openings on the vessel, or the liquid outlet and the solid inlet may share the same openings on the vessel.

[0032] In one embodiment, the use of recycled hydrolysate to pretreat biomass may help increase the concentration of the final hydrolysate. Fig. 2 shows calculations of the concentration of hydrolysates under two different scenarios when assuming that solid residence time is 3 times the residence time of liquid. For instance, where the liquid residence time is 5 minutes, the solid residence time is assumed to be 15 minutes. In Scenario A, the biomass (solids) is not mixed with

hydrolysate, but is loaded into the vessel along with water. In Scenario B, the biomass (mostly dry) is mixed with hydrolysate, instead of water. Under Scenario A, the amount of hydrolysate is calculated as 20x20%=4 kg hemicellulose, and the hydrolysate concentration obtained in Scenario A is 4/(80+60)=29 g/L. By contrast, the hydrolysate concentration obtained in Scenario B is 4/(80+60-80)=67 g/L. Thus, the hydrolysate concentration obtained in Scenario B would be much higher than that of Scenario A.

[0033] As used herein, the term "flowthrough" refers to a process wherein a liquid is added to or mixed with a solid or a semi-solid material and is incubated with the material for a period of time before leaving the solid or semi-solid material. During the course of the flowthrough, the liquid may solubilize, extract or otherwise bring along certain components of the biomass. Flowthrough pretreatment is distinguished from all other pretreatment configurations because the liquid phase could have a shorter residence time in the reactor than does the solid phase. Methods for reducing energy consumption and for effectively extracting usable sugar substrate from biomass are disclosed.

[0034] The term "biomass" generally refers to non-fossilized renewable materials that are derived from or produced by living organisms. For purpose of this disclosure, biomass may include animal biomass, plant biomass, and human waste and recycled materials, among others. Examples of animal biomass may include animal by-product and animal waste, etc. Plant biomass may be any plant-derived matter (woody or non-woody) that is available on a sustainable basis. Plant biomass may include, but is not limited to, agricultural crop wastes and residues such as corn stover, wheat straw, rice straw, sugar cane bagasse and the like, grass crops, such as switch grass and the like. Plant biomass may further include, but is not limited to, woody energy crops, wood wastes and residues such as trees, softwood forest thinnings, barky wastes, sawdust, paper and pulp industry residues or waste streams, wood fiber, and the like. In urban areas, plant biomass may include yard waste, such as grass clippings, leaves, tree clippings, brush, etc., vegetable processing waste, as well as recycled cardboard and paper products.

[0035] The term "vessel" refers to a container or reactor that holds the biomass and one or more other reactants, wash liquid, or enzymes, among others. The

terms "vessel," "reactor," "reaction vessel," "biomass container," and "pretreatment vessel" may be used interchangeably in this disclosure.

EXAMPLES

[0036] The following examples are provided for purpose of illustrating the instant disclosure and are not meant to be limiting.

Example 1 Continuous flowthrough pretreatment under different temperature gradients

[0037] Various parameters, such as oligomer concentration, xylan hydrolysis conversion, and concentration of the degradation product, are compared for a counter-current and a co-current flowthrough system. Fig. 3 shows the results from a counter-current flowthrough system. Fig. 4 shows the same set of measurements when co-current flowthrough is used. Five scenarios of temperature gradients are used: (1) 130 -220 °C; (2) 150-220 °C; (3) 170-220 °C; (4) 190-220 °C; and (5) 220-220 °C, all with temperature increasing from the side of the hydrolysate outlet. A kinetic model is used to determine xylan hydrolysis and oligomer degradation during flowthrough pretreatment. Panels (a) of Figs. 3 and 4 show oligomer (O) concentration along the reactor axis (Z, dimensionless, increases from the side of hydrolysate outlet). Panels (b) of Figs. 3 and 4 show xylan hydrolysis conversion (C) along the reactor axis. Panels (c) of Figs. 3 and 4 show the concentration of degradation product (DP) along the reactor axis. As shown in Figures 3 and 4, higher xylan conversion is likely to be achieved for smaller temperature gradient when either counter-current or co-current flowthrough is used. However, smaller temperature gradient may also result in higher oligomer degradation.

[0038] For each temperature gradient, especially for smaller temperature gradient, oligomer degradation may be much higher for co-current pretreatment as compared to counter-current pretreatment. As shown in Fig. 3, although smaller temperature gradient may result in higher oligomer concentration at the outlet, smaller temperature gradient is also associated with higher degradation of the oligomers. For instance, Fig. 3(c) shows that DPI and DP 2 both have less than 10%, or even less than 5% degradation as compared to higher degradation rate in DP3, DP4 and DP5. Taken together, counter-current pretreatment may yield higher carbohydrate

concentration in the flowthrough hydrolysate and may cause less loss of xylan into degradation product as compared to co-current system.

[0039] In another aspect, as shown in Fig. 5, maintaining a temperature gradient along the reactor axis is advantageous as compared to a fixed reactor temperature. As shown in Fig. 5, for a given final xylan conversion at 90%, countercurrent pretreatment resulted in 66% less degradation of dissolved xylan as compared to co-current pretreatment. For countercurrent pretreatment to reach the same final xylan conversion, maintaining a temperature gradient along the reactor axis reduced xylan degradation by another 12% as compared to a fixed reactor temperature.

CLAIMS

We claim:

1. A system for pretreatment of biomass, said system comprising:

(a) a vessel comprising a solid inlet, a solid outlet, a liquid inlet and a liquid outlet, wherein said biomass enters said vessel through said solid inlet and flows in said vessel from said solid inlet towards said solid outlet, and wherein said liquid enters the vessel through said liquid inlet and flows in said vessel from said liquid inlet towards said liquid outlet and exits said vessel through said liquid outlet as a hydrolysate, said liquid making contact with said biomass as said liquid and said biomass flow inside said vessel,

and

(b) a means for conveying said hydrolysate from said liquid outlet back into said vessel.

2. The system of claim 1, wherein said liquid and said biomass flow in opposite directions inside said vessel.

3. The system of any one of the preceding claims, wherein the solid inlet and the liquid outlet share the same opening on said vessel.

4. The system of any one of the preceding claims, wherein the solid outlet and the liquid inlet share the same opening on said vessel.

5. The system of any one of the preceding claims, wherein said means for conveying said hydrolysate is a conduit through which said hydrolysate flows.

6. The system of any one of the preceding claims, wherein said conduit is an integral part of said vessel.

7. The system of any one of the preceding claims, further comprising a first heating means for heating said hydrolysate as it flows through said conduit.

8. The system of any one of the preceding claims, further comprising a second heating means, said second heating means generating a temperature gradient in said vessel, with temperature increasing from said solid inlet to said solid outlet.

9. The system of any one of the preceding claims, wherein said temperature gradient is in the range of from 20°C to 240°C.

10. The system of any one of the preceding claims, wherein said temperature gradient is from 130°C to 220°C.

11. A method for pretreatment of biomass, said method comprising:

(a) mixing in a vessel an amount of said biomass with a first inflow, wherein said first inflow is a liquid, said biomass and said first inflow flow in opposite directions in said vessel,

(b) obtaining a first effluent as said first inflow exits said vessel after making contact with said biomass, and

(c) allowing said first effluent to pass through a conduit and enter said vessel as a second inflow.

12. The method of claim 11, wherein said steps of (a)-(c) are repeated for at least 10 times.

13. The method of any one of the preceding claims, wherein said first effluent comprises a hydrolysate of said biomass.

14. The method of any one of the preceding claims, wherein said biomass enters said vessel through a solid inlet, flows through said vessel and exits said vessel through a solid outlet after making contact with said first or second inflow.

15. The method of any one of the preceding claims, wherein the mass flow rate of said biomass is at least 2 times slower than the flow rate of said first or second inflow.

16. The method of any one of the preceding claims, wherein said vessel comprises a heating means for generating a temperature gradient in said vessel.

17. The method of any one of the preceding claims, wherein the lowest temperature in said temperature gradient is 20°C or higher, and the highest temperature in said temperature gradient is 240 °C or lower, with temperature increasing from said solid inlet to said solid outlet.

18. The method of any one of the preceding claims, wherein said highest temperature in said temperature gradient is 220°C or lower.

Fig. 1

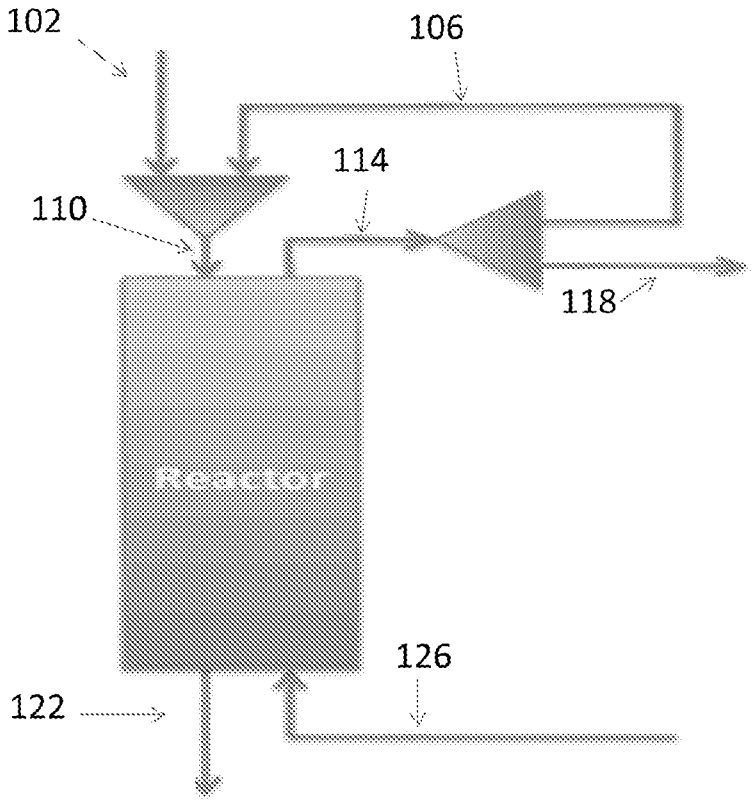
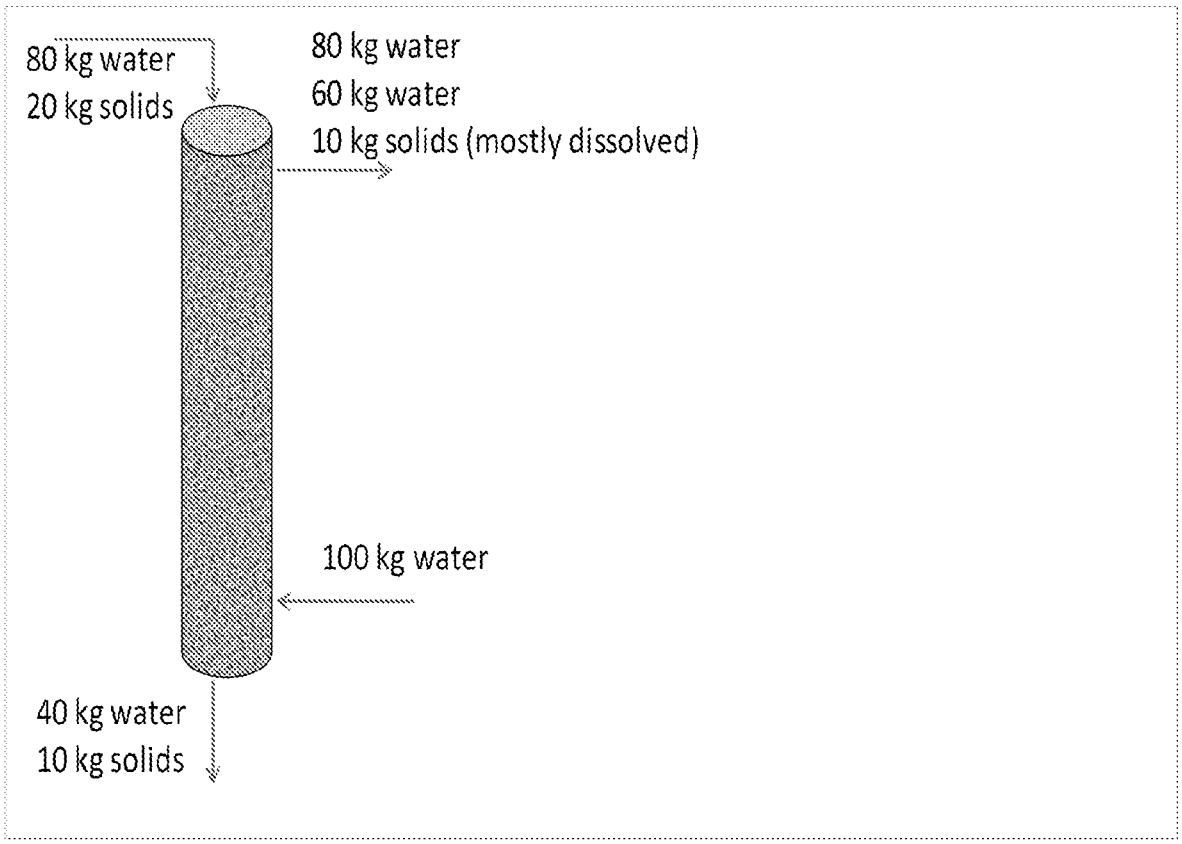


FIG. 2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80 kg water
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10 kg solids (mostly dissolved)
100 kg water
40 kg water
10 kg solids

FIG. 3

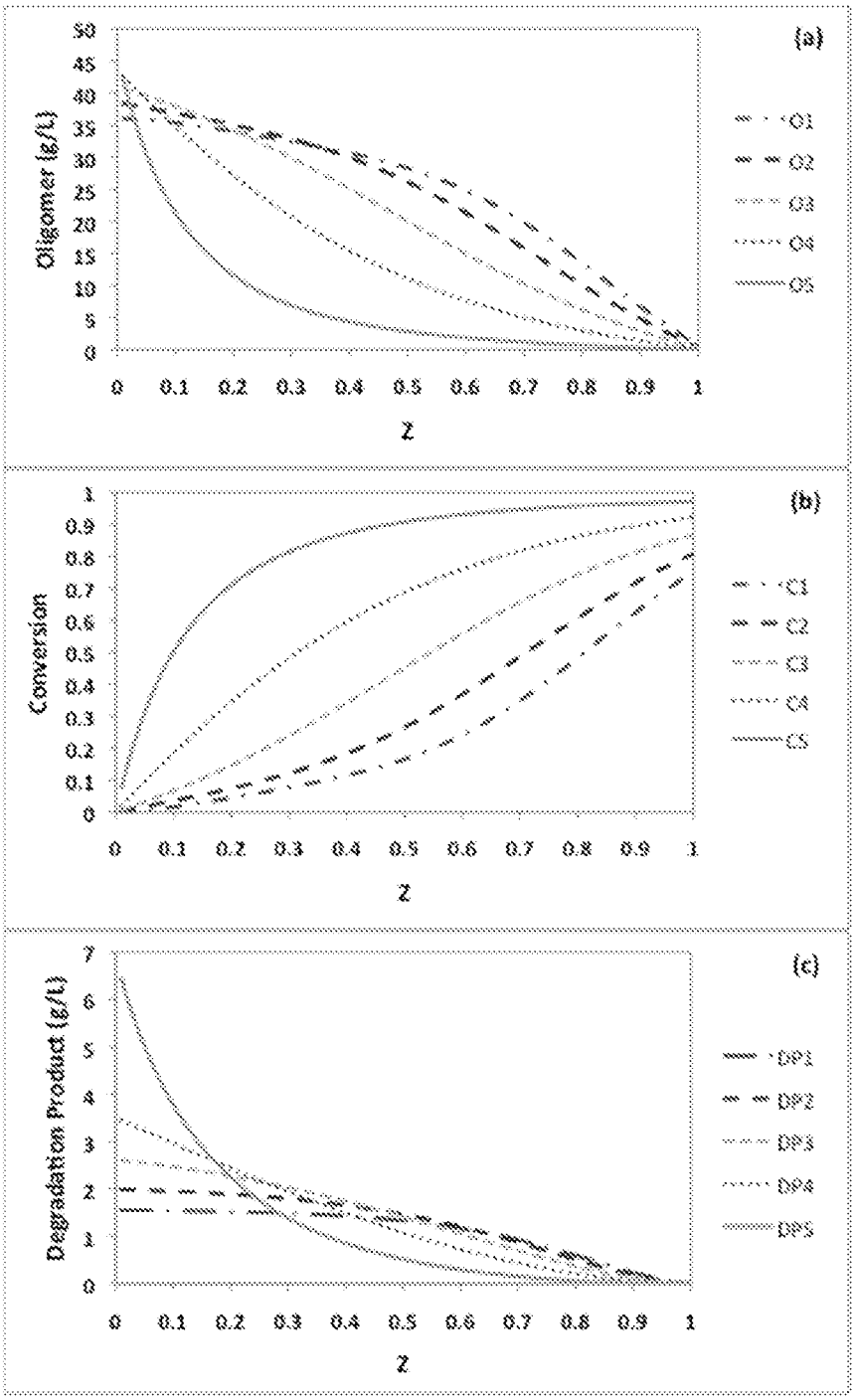
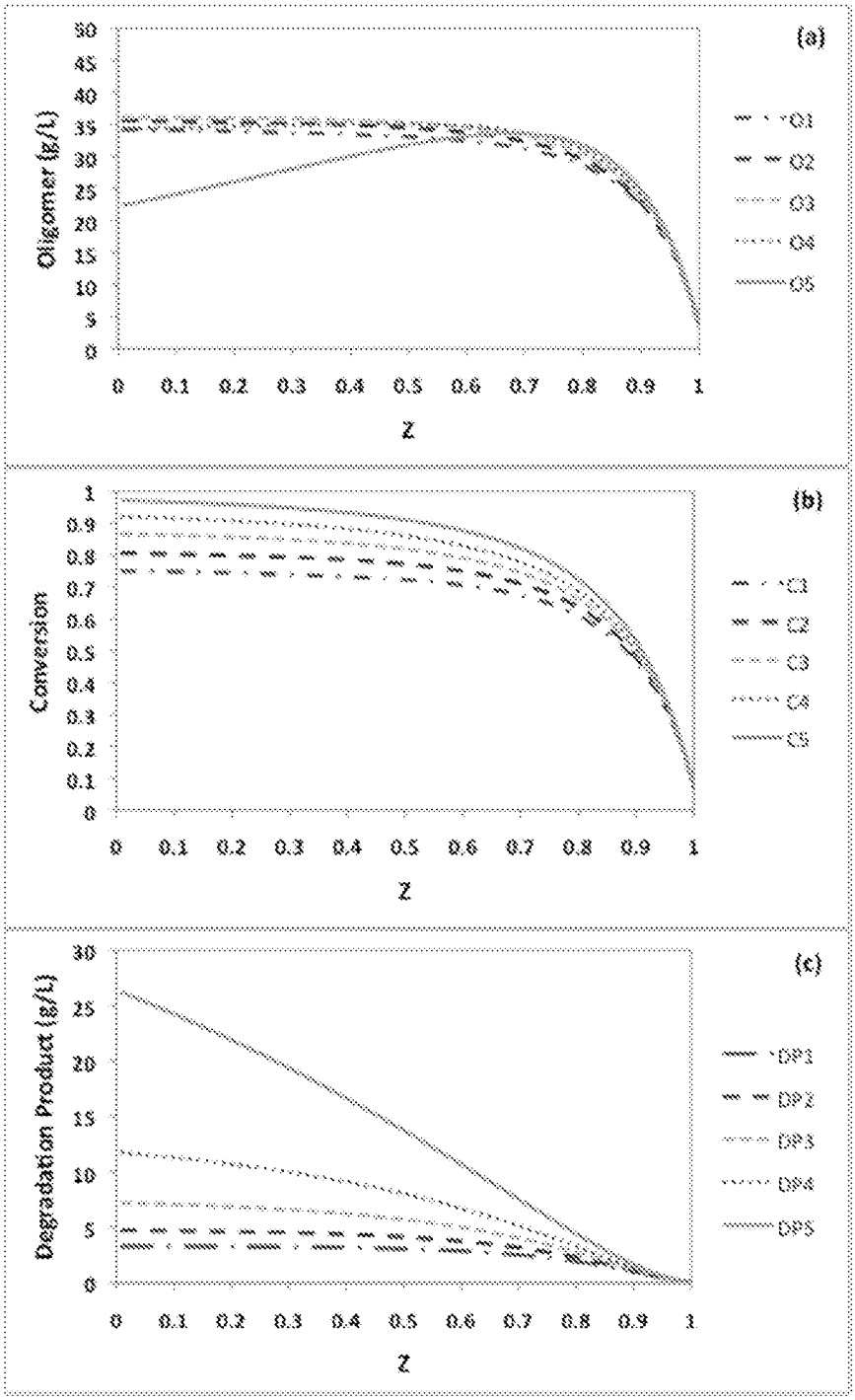

(a)
Oligomer (g/L)
Z
O1
O2
O3
O4
O5
(b)
Conversion
Z
C1
C2
C3
C4
C5
(c)
Degradation Product (g/L)
Z
DP1
DP2
DP3
DP4
DP5

Fig. 4


(a)
Oligomer (g/L)
Z
O1
O2
O3
O4
O5
(b)
Conversion
Z
O1
O2
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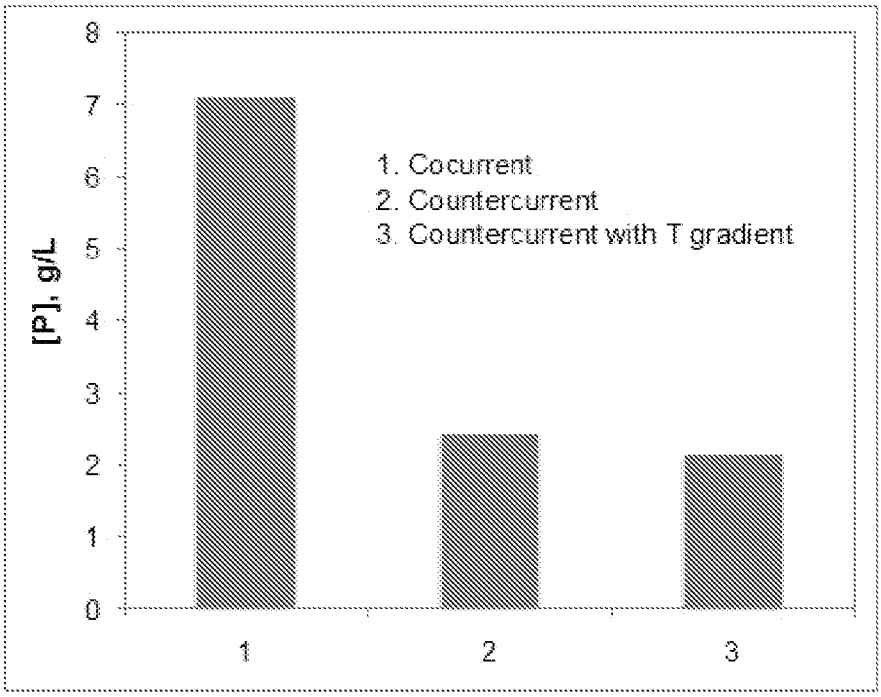
O5
(c)
Degradation Product (g/L)
Z
DP1
DP2
DP3
DP4
DP5

FIG. 5


8
7
6
5
4
3
2
1
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2. Countercurrent
3. Countercurrent with T gradient
1
2
3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/069848

A. CLASSIFICATION OF SUBJECT MATTER

BOIJ 7/00(2006.01)i, C07C 31/08(2006.01)1, BOIJ 19/24(2006.01)1, CIOG 3/00(2006.01)1, CIOL 1/02(2006.01)1

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)

BOIJ 7/00; C12M 1/00; D21C 1/00; D21C 1/06; C12P 13/04; D21C 1/04; D21C 3/02; C13K 1/02; D21C 3/20

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: hydrolysate, biomass, pretreatment, carbohydrate, lignin, countercurrent

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011-0003348 Al (GENTA, M. et al.) 06 January 2011 See abstract ; claims 1, 4; paragraphs [0021], [0022], [0043], [0048], [0049]; figure 1.	1-3, 11-12
X	US 4941944 A (CHANG, R. P.) 17 July 1990 See abstract ; columns 2-6 ; figure 1.	1-3, 11-12
X	WO 2011-028554 Al (ABENGOA BI0ENERGY NEW TECHNOLOGIES, INC. et al.) 10 March 2011 See abstract ; claims 230-234 ; paragraphs [0010], [0015], [0016], [0066], [0156H0158].	1-3, 11-12
A	US 4668340 A (SHERMAN, M. I.) 26 May 1987 See abstract ; figure 1.	1-3, 11-12
A	US 4436586 A (ELMORE, C. L.) 13 March 1984 See abstract ; figure 1.	1-3, 11-12
A	JP 2009-022180 A (OJI PAPER CO., LTD.) 05 February 2009 See abstract ; claims 1, 5.	1-3, 11-13

☐ 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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"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	Date of mailing of the international search report
19 April 2013 (19.04.2013)	**22 April 2013 (22.04.2013)**

Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-70 1, Republic of Korea Facsimile No. 82-42-472-7140	KIM, Seung Beom Telephone No. 82-42-481-3371

Form PCT/ISA/210 (second sheet) **(July** 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/069848

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: **13**
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

Claims 1-10 relate to a system, but claim 13 dependent on claims 1-10 relates to a method. As claim 13 does not clearly define the matter for which protection is sought, this claim does not meet the requirement of PCT Article 6.

3. ☒ Claims Nos.: **4-10, 14-18**
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. Ill Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2012/069848

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