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- (73) Patenthaver: **CH-Bioforce Oy, Ahventie 4 A 21-22, 02170 Espoo, Finland**
- (72) Opfinder: **Von Schoultz, Sebastian, Levontie 197, 21600 Parainen, Finland**
- (74) Fuldmægtig i Danmark: **Plougmann Vingtoft A/S, Strandvejen 70, 2900 Hellerup, Danmark**
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Fortsættes ...

DESCRIPTION

Field of the invention

[0001] The present invention relates to a method for extracting sugars and derivatives thereof and the corresponding polysaccharides especially hemicelluloses from lignocellulosic biomass with hot water. In particular the present innovation concerns a method to produce high concentration of high purity hemicellulose extract with minimal use of water. The extract is circulated through the biomass several times and as a result the concentration of the hemicelluloses in the water phase is increased. The circulating loop is vital in order for the non-hemicellulose material, such as lignin, to be adsorbed back to the biomass. The circulation also enables gentle extraction conditions regarding temperature, pressure and pH as the method does not require maximum extraction during the first extraction loop. Minimal oxidation and degradation of the hemicelluloses is achieved by removing virtually all of the air and especially oxygen gas from inside of the pores of the biomass during a impregnation step assisted by reduced pressure. The concentration of the extract is increased by using the same extract in several extractions of new and previously un-extracted biomass.

Description of Related Art

[0002] Wood based biomass contains about 25% of hemicelluloses. Extraction of biomass is a very well known process and has traditionally been extracted with alkali. During this kind of treatment hemicelluloses are degraded and the fibrous material is decomposed.

[0003] Traditional extraction with only hot water degrades the sugars into toxic compounds such as furfural.

[0004] Steam explosion is another well known method for extracting carbohydrates from biomass. However, even this method involves the formation of toxic compounds.

[0005] A recent method for extracting hemicelluloses from biomass involves continuous flow of hot water extraction. The problem with this method is, that it produces a very diluted extract containing up to 30% lignin impurities (WO 2009/122018 and Leppänen et al.: Pressurized hot water extraction of Norway spruce hemicelluloses using a flow-through system, Wood Sci Technol (2011) 45:223-236)

[0006] All the known extraction methods of hemicelluloses results in extremely low solids content of the extract, and require expensive concentration of the extract. This results in an economically unsound product for transport and further treatment. (WO0034568, US2008029233, US8136747, DE3225074).

[0007] A recent patent publication WO2007090926 describes a method for recovering hemicelluloses with higher concentration through steam hydrolysis. The drawback with this approach is that hydrolysis always involves deacetylation of the hemicelluloses which effectively lowers their water solubility and also degrades the polymers by lowering the molar mass. Chemical and food industry are interested in polysaccharides with high molar mass which the aforementioned method is unable to provide.

[0008] Publication WO0061276 discloses a method for hydrolysis of hemicelluloses primarily into monomeric sugars which is a drawback especially if polymers are desired.

[0009] The main problem with known methods is the fact that they do not efficiently prevent oxidation, hydrolysis, degradation and deacetylation of the biomass. Especially the presence of air and oxygen gas inside of the pores of the biomass has prevented an efficient and gentle extraction procedure. Traditionally biomass impregnation and air removal from inside of biomass capillaries has been for example achieved through presteaming of biomass with high temperature steam and high pressure. However, this procedure causes oxidation and hydrolysis of hemicelluloses and is therefore unsuited for extracting hemicelluloses without degradation.

Summary of the Invention

[0010] It is an aim of this invention it to overcome the problems related to known art and to provide an improved method for extracting biomass with water.

[0011] In particular, it is an aim of the invention to provide a method which effectively minimizes oxidation and degradation of the biomass extract.

[0012] It is further an aim to provide a method to concentrate and purify the extract with minimal water consumption, without the need for expensive evaporation and purification steps.

[0013] More specifically, the method according to the invention is characterized by what is stated in claim 1.

Detailed Description of the Invention

[0014] The present invention is based on the finding that air and more specifically oxygen gas causes severe oxidation and degradation of sugars and polysaccharides at high temperatures. Reducing the air pressure inside of a reactor containing biomass, following the filling of the reactor with water effectively fills the capillaries of the biomass resulting in an almost completely oxygen free environment inside of the biomass.

[0015] The present invention is further based on the finding that recirculation of the extract through the biomass purifies the extract from unwanted compounds such as lignin and other polyphenols. The presence of phenolic substances such as lignin in the extract lowers the capacity of microbes to digest polysaccharides and therefore the production of biofuels becomes less economical.

[0016] The method according to the invention allows a long time for the extract to be kept at high temperatures without significant oxidation and degradation of the molecules and polymers in the extract. This further allows the extract to be reused for extraction of un-extracted biomass which enables the consistency of the extract to be increased significantly without evaporation of the solvent.

[0017] By removing hemicelluloses from the fiber fraction the energy value and the lignin content of the biomass increases. At the same time the fiber fraction properties become more suitable for the making of pellets and chipboards.

[0018] Therefore, present invention comprises of the steps:

- Feed the biomass into an reactor
- Remove most of the air and oxygen gas from the biomass by reducing the pressure inside of the reactor
- Impregnate the biomass with the extraction water. During the first extraction this is plain water and in later extractions this is the extract from the previous extraction
- Start circulating the extraction water through the biomass
- Increase the temperature to extraction temperature
- Circulate the extraction fluid until desired consistency and purity is reached
- Remove the extraction water from the reactor
- Remove the biomass from the reactor
- Start over from the first step

Examples

[0019] The effect of extract circulation and impregnation under reduced pressure (0.8 Bar under pressure) was investigated. The biomass was 200 grams (O.D.) of Scott spine chips (*Pinus Sylvestris*). The water to wood ration was 5:1. The extraction water was kept at 150°C for two hours. In experiments with circulation, the extract had circulated 10 times through the biomass. The pH of the extract was measured every half hour. In experiments where the biomass was impregnated, hence most of the air and oxygen gas was removed from the reactor, no changes in pH could be noted. In experiments without impregnation under reduced pressure a significant pH drop, typically over one pH unit was recorded. This indicated that the formation of acids, especially through deacetylation of the biomass did not occur in the

experiments with impregnation. The yield of the extractions is shown in Figure 1. The extracts were analyzed by gas chromatography for carbohydrates (SundbergA, SundbergK, Lillandt C, HolmbomB (1996) Determination of hemicelluloses and pectins in wood and pulp fibers by acid methanolysis and gas chromatography. Nord Pulp Pap Res J11(4):216-219) and lipophilic extractives (F. Örså, B. Holmbom and J.Thornton, Wood Sci. Technol. 31 (1997) 279). Lignin was determined according to the method by Iiyama et al. (Iiyama, K.; Wallis, A. F. A. An improved acetyl bromide procedure for determining lignin in wood and wood pulps. Wood Sci. Technol. 1988, 22, 271-280). The samples without impregnation and circulation contained 55% hemicelluloses, 35% lignin and 5% lipophilic extractives and 5% unidentified. Samples without impregnation and with circulation contained 90% hemicelluloses, 1.5% lipophilic extractives and 8.5% unidentified. Samples with impregnation and circulation contained 96% carbohydrates and 0.5% lipophilic compounds. The remaining 3.5% was unidentified. The results clearly show that the circulation removes most of the initially released lignin and extractives. The impregnation and air and oxygen removal procedures clearly increase the extraction yield and reduce the amount of unidentified components which are most likely oxidized lignin fragments. By comparing the extract composition when using both impregnation and circulation with an extract produced according to the method described in WO2009122018, we can clearly see the benefits of using the method described in this document (Figure 2). This method produces an extract without unwanted impurities, especially lignin.

[0020] Figure 1 shows the extraction yield of six different extractions:

- two without impregnation under reduced pressure and without circulation of extract
- two without impregnation under reduced pressure but with circulation of the extract
- two with impregnation under reduced pressure and circulation of the extract.

[0021] Oxidation of the extracted components was prevented by keeping the extract in oxygen gas reduced environment. Extracting under minimized presence of oxygen gas produces a clear yellow and transparent extract. However, if the extract comes in contact with oxygen gas, it turns dark brown within minutes and the oxidization will continue even at room temperature. Extracts which were removed from the reactor into nitrogen saturated environment did not show signs of oxidization nor did the color of the extract change.

[0022] By reusing the extract from previous extraction the consistency of the extract could be increased significantly by each batch without any significant changes in the pH of the extract or the molar mass and composition of the carbohydrates. Figure 3 shows the consistency increase of the extract by reusing the extract.

REFERENCES CITED IN THE DESCRIPTION

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- **F. ÖRSÄB. HOLMBOMJ.THORNTON** *Wood Sci. Technol.*, 1997, vol. 31, 279- [0019]
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Patentkrav

1. Fremgangsmåde til behandling af biomasse indeholdende fiberholdig struktur og polysaccharider, omfattende:

- 5 - at udsætte biomassen for en ekstraktiv behandling hvor den opvarmes i vandig fase ved et tryk under 800 kPa (8 bar) og ved en temperatur under 160 °C for at separere polysacchariderne fra biomassen;

kendetegnet ved, at

- 10 - biomassen imprægneres med ekstraktionsvandet under reduceret tryk, på mindst 30 kPa (0,3 bar) under tryk, forud for ekstraktion;
- ekstraktet recirkuleres kontinuerligt gennem biomassen for at holde oxygengasniveauet på et minimum gennem hele ekstraktionen;
- det polysaccharid-rige ekstrakt separeres fra biomassen ind i omgivelser med reduceret oxygengas som en første fraktion;
- 15 - den fiberholdige struktur af biomassen genvindes som en anden fraktion;
- ekstraktet genanvendes til ekstraktionen af ikke-ekstraheret biomasse;
- og
- mindst en af fraktionerne udsættes for yderligere behandling.

20 **2.** Fremgangsmåde ifølge krav 1, hvor the kulhydratekstraktet separeres fra i form af oligomerer og polymerer.

3. Fremgangsmåde ifølge krav 2, hvor kulhydratekstraktet hydrolyseres eller anvendes som næring til mikrober i fremstillingen af brændstof eller som

25 råmateriale til kemiske produkter.

4. Fremgangsmåde ifølge krav 1, hvor den fiberholdige fraktion udsættes for separationen af lignin fra den fiberholdige struktur.

30 **5.** Fremgangsmåde ifølge krav 1, hvor den fiberholdige fraktion anvendes til fremstillingen af papir og pap.

6. Fremgangsmåde ifølge krav 1, hvor den fiberholdige fraktion anvendes til fremstillingen af piller eller som råmateriale til brændstof.

- 7.** Fremgangsmåde ifølge krav 1, hvor den fiberholdige fraktion anvendes til fremstillingen af træfiberplader (spånplader).
- 8.** Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor
5 biomassen er træbaseret, især spåner eller savsmuld, fortrinsvis pressede spåner.
- 9.** Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor biomassen ikke er et træprodukt, især bagasse og halm.
- 10 **10.** Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor biomassen udsættes for ekstraktiv behandling, hvor den opvarmes i vandig fase ved et tryk under 800 kPa (8 bar) og ved en temperatur på ca. 150 °C for at separere polysacchariderne fra biomassen.

DRAWINGS

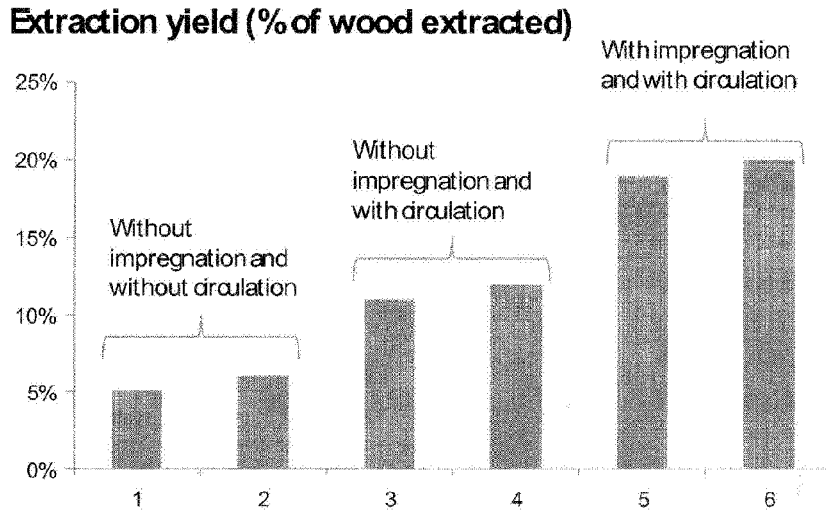


Figure 1. The effect of vacuum impregnation of biomass and circulation of the extraction water.

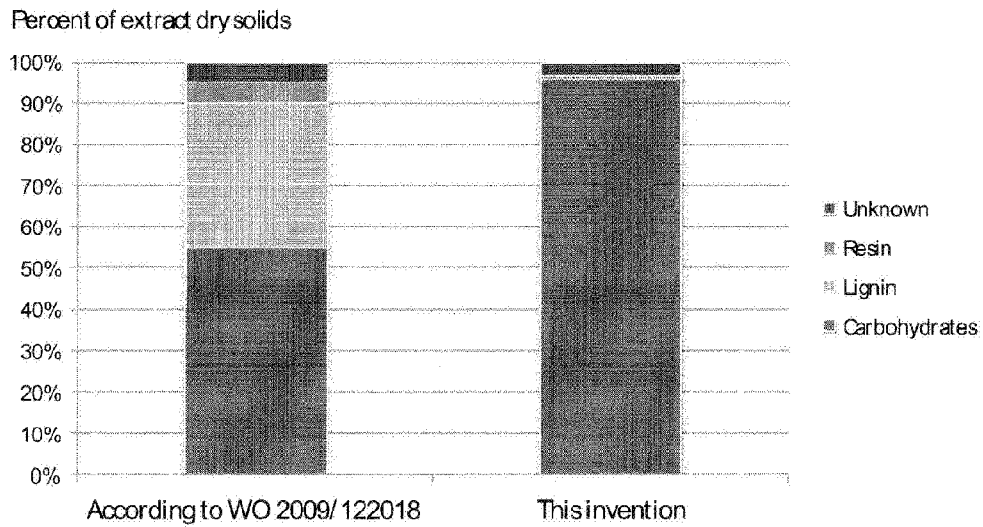


Figure 2. Extract composition according to method described in WO2009122018 and in this invention.

Solids content of extract

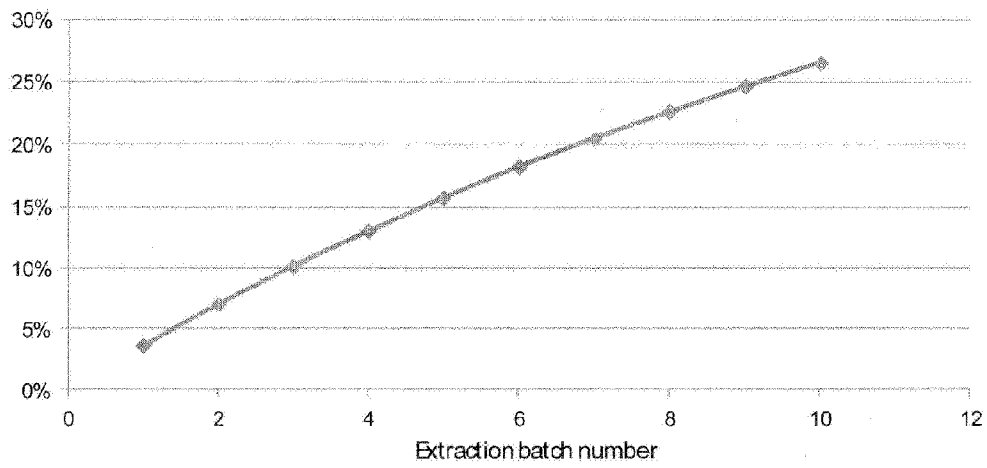


Figure 3. Solids content increase as a result of the reuse of extraction water in multiple extractions.